ELEMENTS

OF

CHEMISTRY,

INCLUDING THE

MOST RECENT DISCOVERIES AND APPLICATIONS OF THE SCIENCE TO MEDICINE AND PHARMACY, AND TO THE ARTS.

BY ROBERT KANE, M.D., M.R.I.A.,

PROFESSOR OF NATURAL PHILOSOPHY TO THE ROYAL DUBLIN SOCIETY; PROFESSOR OF CHEMISTRY TO THE APOTHECARIES' HALL OF IRELAND; MEMBER OF THE SOCIETY OF PHARMACY OF PARIS, AND OF THE GERMAN PHARMACEUTICAL SOCIETY, ETC., ETC., ETC.

AN AMERICAN EDITION,

WITH ADDITIONS AND CORRECTIONS, AND ARRANGED FOR THE USE OF THE UNIVERSITIES, COLLEGES, ACADEMIES, AND MEDICAL SCHOOLS OF THE UNITED STATES,

BY JOHN WILLIAM DRAPER, M.D

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF NEW-YORK, FORMERLY PROFESSOR OF PHYSICAL SCIENCE AND PHYSIOLOGY IN HAMPDEN SIDNEY COLLEGE, VIRGINIA; MEMBER OF THE LYCEUM OF NATURAL HISTORY OF NEW-YORK, &c., &c., &c.

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PREFACE TO THE AMERICAN EDITION.

In preparing the work of Dr. Kane for the use of American students, I have preserved the original entire, and have only made those alterations in it which the system of instruction pursued in the United States seems to require.

This work, which, as a text-book, is undoubtedly the best extant in the English language, representing the present condition of chemical science, necessarily contains much detail. To give it completeness, it was needful to include the description of many bodies of little technical importance, to describe experimental processes, and sometimes to dwell on facts of minor value.

The period of instruction in the schools of this country is short, so that many standard books are unavailable from their extent. From an experience of several years in public teaching, I have perceived the importance of separating, for the student, the leading principles from the accompanying detail. This will, perhaps, to a certain extent, be accomplished by the mechanical contrivance of printing such works with different types, the important matter being in the larger letters.

The magnitude of the original prevented me from making additions to any great extent; what has been introduced in this way will be readily distinguished, from being inserted between brackets.

From its having been repeatedly and carefully read, and the errors and misprints revised, this will probably be found more correct than the foreign edition.

John William Draper.

University of New-York, June 1st, 1842.

PREFACE.

My object in the following pages is to present to the student an account of the general principles and facts of Chemistry, and of its applications to Pharmacy, to Medicine, and to the Useful Arts.

In the arrangement of a work like the present, if the general principles of the science are first described, it is impossible to avoid the difficulty of introducing the names of many substances with whose history the reader cannot be supposed conversant; and by entering, in the commencement, on the description of individual substances, reference to the principles of affinity and the laws of constitution is continually necessary, in order that the reactions of these bodies may be understood. In both cases the student is liable to some embarrassment, but I believe it to be greater in the latter, and hence I have adopted the plan of fully describing all the general principles and laws of chemical action, before entering on the description of the chemical substances in detail.

Chemistry being itself but a department of Natural Philosophy, although the most extensive in its objects and the most important in its uses, it is connected so intimately with the other branches of Physics, that a knowledge of at least their general principles is necessary for the proper understanding of the nature of chemical phenomena. I have consequently embraced within the design of the present work a description of the physical properties of bodies, so far as they serve to complete their chemical history, or influence their chemical relations; and thus, upon the one hand, supply characters by which chemical substances may be recognised, and, upon the other, modify the affinities by which the action of chemical substances upon each other is determined. With this twofold object, the chapters on Cohesion, Light, Heat, and Electricity have been drawn up.

The portion of the work which treats of the general laws of chemical combination, is followed by an account of the mode of preparation and properties of all inorganic substances of interest to Science, to Medicine, or to the Arts. But in this part I will pass over very briefly the history of numerous bodies which, from their rarity, are objects only of

scientific curiosity, referring those who would wish to study their history more closely to the extended works of Thompson, of Graham, of Dumas, or of Berzelius.

In the department of Organic Chemistry my object will be fully to discuss the history of all such bodies as are of importance, from their bearing upon general principles or existing theories, from their use in medicine or pharmacy, their employment in the arts or in ordinary life. The numerous series of bodies which are every day discovered in Organic Chemistry, but which do not come under any of the above heads, shall be dismissed with only a notice of their existence.

The relations of chemical action to the functions of organized matter, the applications of Chemistry to Physiology and to Pathology, will be treated of so far as our accurate knowledge extends; and, finally, a succinct description of the mode of analysis of organic and inorganic bodies will be given.

As this work is not intended to be a complete system of Chemistry, nor to satisfy the wants of those who wish to make Chemistry their special study, I have in almost all cases avoided references or quotations, which would needlessly occupy much space; for, in the larger works already mentioned, the original authorities on all subjects will be found.

The object of a work like the present being to represent faithfully the general aspect and extent of science at the time of publication, its details must be in great part founded on the results of others. Hence originality cannot in any great degree be either expected or desired; but I have not hesitated, in many instances, where the best consideration I could give the subject induced me to dissent from views generally held, to make this work the vehicle, in a popular form, of such suggestions as I thought deserved to be adopted.

The processes given for the preparation of the various substances described are, with very few exceptions, those followed either in my private laboratory or in the manufacturing laboratory of the Apothecaries' Hall of Ireland; and the apparatus figured in the woodcuts are generally similar to those which I employ in experiments of research or at lecture.

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ELEMENTS OF CHEMISTRY.

The science of chemistry has its origin in the principle, that the bodies which constitute the external world are composed of a variety of elements, united according to certain laws. If we could conceive a universe consisting only of iron, or quicksilver, or sulphur, the objects of the astronomer might still remain as extensive and as sublime as they are in the actual state of things; for, in tracing the constitution of planetary and satellitic systems, or reducing to precise laws the forces by which the motions of the heavenly bodies might be produced, all the resources of his science would still be brought into play. In like manner, the physical sciences could attain perfection, for the relations of these bodies to heat, to light, to electricity, the various problems and laws of statical and dynamical forces, could have been known, and thus all that is essential to the science of natural philosophy might be attained. But not even an idea of chemistry could have been formed. The duty of chemistry is to find the constituent elementary substances, which, by uniting, form the various compound bodies which we observe; to ascertain the nature of the forces by which they unite, and the laws by which their union or separation may be regulated; to trace the effects of their mutual action in the properties of the new substances formed by their combination, and in the phenomena, independent of composition, which accompany the exertion of chemical force.

This object of chemistry has been at all periods fully recognised; for the earliest philosophers, even before the science had received a name, considered its objects as well defined in the arrangement of the elements of fire, air, earth, and water. When the methods of chemistry, and the reasonings to which they led, acquired a better form, these elements, which had been assumed from speculations in natural history and metaphysics, gave way to others, as sulphur, spirit, salt, oil, and earth, equally incorrect, but still those which, in the rough trials of the period, were obtained by decomposing compound bodies. As more accurate ideas and better processes were acquired, these elementary principles changed again their character, until, finally, the philosophical idea of chemistry was clearly stated and established by Lavoisier: 1st, that we study to resolve the various compound bodies found in nature into others which resist our power, and which we term *undecompounded or simple substances*, without pretending that they are elements; for the advance of science enables us to decompose, in each generation, bodies which to our own predecessors had appeared simple; 2d, that we study to effect the recombination of those simple bodies,

either in the same proportions, and thus regenerate the natural compound bodies, or in new proportions, and thus add to the catalogue of bodies which may exist in nature.

Of these two operations, the first, or separation of a compound body into the simple substances which constitute it, is termed *analysis*. The second, or combination of simple to form a compound substance, is called *synthesis*. All chemical processes are conducted upon the principle of one or other of these two, and occasionally they are both, successively or synchronously, accomplished.

The objects of chemistry cannot, however, be considered as limited to the mere abstract study of the laws of elementary composition; to it also belongs the improvement of processes in the useful arts by the more accurate knowledge of their theory which chemistry confers, and the invention of new processes or of new arts, by the application or discovery of substances previously neglected or unknown; the alleviation of disease, by new remedies which may be placed at the command of the physician, or by more correct ideas of the origin and results of morbid action, to which the attentive study of the chemical processes of the great laboratory of the human frame may ultimately lead, ranks also among the most important of its applications: and, although an abstract science, which reveals some of the most beautiful of nature's laws, deserves our best attention, yet it becomes invested with more general interest, and commands more universal homage, when, as with chemistry, it appears to be the basis of those practical arts on which so much of health, of national prosperity, and of civilization may depend.

The origin or derivation of the word *chemistry* is unknown. It was first found as χημεία, indicating the art of making gold and silver among the Egyptians and Greeks of the Empire, at the commencement of that extraordinary perversion of the idea of elementary constitution which fascinated mankind for nearly five hundred years. From the Greeks it was naturally adopted, with the vain pursuit which it denoted, by the Arabians, and, passing with the Arabic prefix into the languages of modern Europe, became *alchemy*. When the just objects and powers of the science were finally recognised, it was termed *chemia* or *chemistry*.

In studying those properties of the different kinds of matter by which they are recognised to be distinct and independent chemical substances, it is unavoidable to include those qualities which, although common to all forms of matter, yet differ in degree among the different kinds, and thus serve as distinguishing characteristics of them. The physical properties of various bodies are hence in common use among chemists, as serving to perfect their description; and, indeed, the limit between properly physical and properly chemical properties of substances is not always capable of being distinctly drawn.

CHAPTER I.

OF GRAVITY AND COHESIVE FORCES AS CHARACTERIZING CHEMICAL SUBSTANCES.

THE physical forces which are of most importance in determining the characteristic properties of bodies are gravity and cohesion. These differ, however, remarkably in principle from each other, and are applied to quite independent purposes. Gravity is common to all forms of matter, and is totally independent of its nature. It is exerted at all, even the greatest conceivable distances, and is the invisible yet insuperable tie, which, connecting together the satellites and planets of our system with the central sun, assigns to each of the tenants of our boundless skies its place and motions. Acting thus only on the mass, gravity is a measure of the quantity of matter present in a body; and what we term weight is only the gravitating force exerted by the substance which we weigh. By no natural operation can the smallest particle of matter be annihilated or destroyed; throughout the most complicated processes the quantity of matter remains constant, and hence we are enabled to verify the accuracy of our chemical operations, by proving the weight of the bodies ultimately formed to be equal to the weight of the substances by whose action they have been produced.

Under the same volume different bodies have very different weights, and hence contain different quantities of matter. Bodies are said to be more or less *dense*, according as in a given bulk they contain a greater or less quantity of gravitating matter; and when a certain body is taken as a standard, and their density reduced to numbers, there is obtained the *specific gravity* of each body, or the comparative quantity of matter it contains in a given bulk, which, being almost always the same for the same body, is an important element in its history, and may often serve for its recognition.

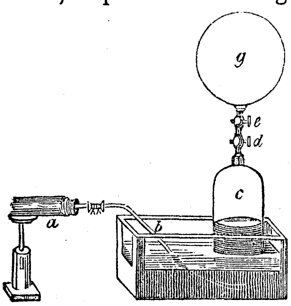
The determination of specific gravities is easily performed where the volume of the substance can be exactly measured. Thus for liquids, as water, oil of vitriol, or alcohol: if a small bottle be taken containing an ounce of water, or 480 grains, it will contain 343 grains of sulphuric ether, or 885 grains of sulphuric acid. Now the densities will be as these numbers; or water being taken as the standard, and its specific gravity being assumed as 1000, the specific gravities of the others become proportional to it; as,

Water . . .	480 :	1000
Ether . . .	343 :	715
Sulphuric acid	885 :	1845

To save this little calculation, the bottle in use is generally made to hold 1000 grains of pure water, and then, filling it with the fluid to be tried, the weight gives directly the specific gravity.

Where the substance exists naturally in the state of gas, a precisely similar process may be had recourse to; in place of a bottle

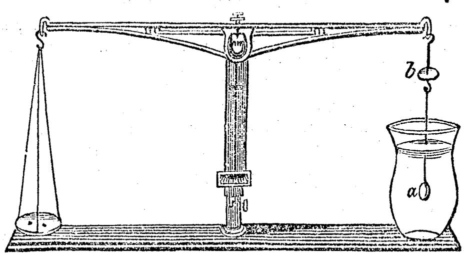
with a ground glass stopper, there is used a globe, g, with a stop cock, capable of holding from twenty to thirty cubic inches. A quantity of air having been removed from the globe, the gas, which must previously be either perfectly dried or perfectly saturated with moisture, is admitted to supply its place; and as the volume of gas which passes in is exactly equal to the volume of air which had been taken out, the relative weights give their densities, and hence the specific gravity of the gas. For, suppose that the globe full of air weighed 656 grains; that, having been exhausted of air, it weighed 647·5, and then, having received 28 cubic inches of carbonic acid gas, it weighed 660·3 grains. We thus know that the 28 cubic inches of air had weighed 8·5 grains, and that 28 cubic inches of the gas had weighed 12·8; hence the densities are as 8·5 to 12·8, and the specific gravity of the gas, air being taken as 1000, is $\frac{12 \cdot 8}{8 \cdot 5} \times 1000 = 1 \cdot 506$.



This brief description being intended only to explain the principle which the words "specific gravity" involve, it has been considered as not liable to alteration; but, in reality, the volumes of bodies, particularly of gases, are constantly in a state of change. According as the air is warmer or colder; according as the pressure to which it is subjected, as indicated by the barometer, diminishes or augments, the volume which a certain weight occupies is altered, and the specific gravity is changed. Hence, when we take air as a standard of specific gravities for gases, we do so only with reference to a certain standard of temperature and pressure, as at 32 on the scale of Fahrenheit's thermometer, and at 30 inches of mercury in the barometer tube. It is only by accident that an experiment might happen to be made at this standard temperature and pressure, and hence it is necessary to reduce the observed result to what the result should have been at the standard points. If the gas be damp, it is necessary also to correct for the presence of the watery vapour, and hence the determination of the specific gravity of a gas, although so simple in theory, is in practice a most delicate operation. Under the proper heads of the constitution of gases and vapours, with regard to heat and pressure, the mode of making these corrections will be described.

The determination of the specific gravity of a solid body involves in practice some principles in addition to those above stated. We cannot regulate the bulk of a solid body as we wish, and hence the volume must be determined indirectly. This is done by finding how much water it displaces. Thus, if the solid be in many small fragments, weighing altogether, for example, 357 grains, they may be introduced into a specific gravity bottle containing 1000 grains of water. A quantity of water overflows exactly in bulk to the solid which is introduced. The bottle being full, the solid body and the remaining water are then found to weigh 1285 grains. Now, if no water had been expelled, the water and solid body should have

weighed 1357 grains. The difference 72 is the weight of the water expelled; and, consequently, the weights of equal volumes, or the densities of the water and of the solid, are as 72 and 357; or, the specific gravity of the water being taken as 1000, that of the solid is $\frac{357}{72} \times 1000$, or 4958. If the solid be unsuited for that method, its volume is next determined by the principle that a solid body immersed in a fluid is partly supported by the upward pressure of the liquid which it displaces. The solid, in order to sink in the liquid, has to displace and push upward a quantity of it equal to its own bulk, and to resist its weight or tendency to sink down again; for this purpose a portion of the weight of the solid must be employed, and it is only the overplus that is counterpoised by the weights when we proceed to weigh the solid body immersed in any fluid. A solid weighs, therefore, less when immersed in a fluid than when weighed in the ordinary manner, the difference being the portion of the weight of the solid which is employed to sink it, or to resist the force of the liquid which tends to float it up, and this is equal to the weight of the liquid which the solid pushes out of its place, and which is of the same volume as the solid. To effect this operation, a balance, as in the figure, is taken, generally with one scale dish. The solid is hung to the other extremity of the beam by a fine hair or thread of cocoon-silk, *b*, and is thus weighed as usual; let us suppose that it weighed 295 grains.



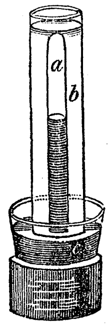
A vessel of pure water is then so arranged that the solid shall be immersed as nearly as possible in the centre of it (as *a* in figure), and it, being then again weighed, is found to be lighter than before; let us suppose that it shall weigh 243 grains. This is the overplus of its weight after having neutralized the tendency of the water to float it up. The difference of the two weighings 295—243=52 grains is therefore the amount of the upward pressure, or the weight of the water which the solid displaced. Equal volumes thus of the solid and of the water are found to weigh respectively 295 and 52 grains, and the comparison of these numbers, water being taken as 1000, gives the specific gravity of the solid, which is $\frac{295}{52} \times 1000 = 5673$.

A variety of other instruments are made use of for measuring the specific gravities of solids and of fluids, as areometers, hydrometers, &c.; but as here it is rather the general principles than the practical details of such operations that are of importance, I shall not enter into their description.

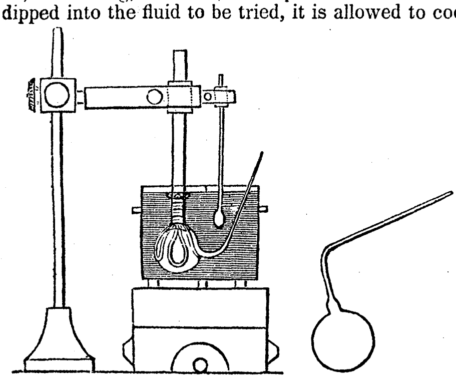
The specific gravity of compound gases is found to have a highly important relation to their ultimate constitution, and throws great light upon some of the most general laws of chemistry; but as yet, notwithstanding some interesting specula tions of Perzoz and of Boullay which I shall hereafter notice, no connexion be

tween the chemical properties or composition of liquid or solid bodies and their specific gravities has been discovered. The physical constitution of vapours and gases being, however, identical, those bodies which, being volatile, are capable of assuming the form of vapour, may render, by the examination of the specific gravities of their vapours, most interesting indications of the manner in which their elements are combined, and methods of performing this operation have been contrived by some of the most illustrious of chemists, as by Dumas and by Gay Lussac.

The method of Gay Lussac is the simpler of the two, and, for substances which are volatilized at moderate temperatures, easily applied. A basin, *c*, is taken, which rests upon a little furnace, and contains mercury. In this basin the graduated bell glass, *a*, is inverted full of mercury. Let us suppose we wish to determine the specific gravity of vapour of water. One or two little bulbs are taken and filled with water as follows: the bulb is warmed with a lamp, and allowed to cool with the point dipped into the water; in this manner a little water gets admission; this is then boiled in the bulb until all air has been expelled, and the bulb is filled with pure steam; the point being then dipped under the surface of the water, as the steam condenses, the water rushes up to supply its place, and the whole becomes full; the point being then touched to the flame of a lamp, it is melted, and the orifice is closed. A small quantity, three or four grains, of water being thus enclosed, the little bulbs are passed under the edge of the jar, *a*, and rise to the top, where they float upon the mercury; a glass cylinder, *b*, open at both ends, is now placed round the jar, resting on and secured to the dish, *c*, and into it is poured so much colourless oil as shall completely cover the jar, *a*, but allow of the graduation being distinctly seen; the furnace is then lighted, and as the temperature of the oil and mercury rises, the water in the little bulbs forms steam, which at last bursts the bulbs, and the level of the quicksilver in the jar immediately falls, the steam occupying the space above it. When the mercury ceases to descend, it is known that all liquid has been converted into vapour; the temperature of the oil, which is necessarily the same as that of the vapour inside, is ascertained, and by the graduation on the jar the volume occupied by the vapour is accurately read off; the weight of the vapour is known, for it is the weight of the water in the bulbs, and its volume at this high temperature is thus found. Knowing thus the volume of a few grains of steam at 250°, the volume at 32° may be calculated; and as the volume of so many grains of air at 32° is already known, the specific gravity of the vapour of water is obtained. The temperature of the oil must be at least thirty or forty degrees above the boiling point of the liquid, and hence it is likely to become coloured, to fume, or even to risk taking fire, unless great caution is employed.



The method invented by Dumas has the advantage of being applicable to all temperatures below the melting point of glass, and it is consequently by its application that the greatest benefit has been conferred on science. It is, however, more complex in principle, though not less delicate in practice. A globe holding from ten to fifteen cubic inches, and drawn out at its beak to a capillary orifice, is carefully weighed, containing, as usual, atmospheric air. It is then warmed, and its beak being dipped into the fluid to be tried, it is allowed to cool, until by the contraction of the air a sufficient quantity of the fluid has made its way in. The globe is then fitted in a sort of cage, by which it is securely held in the centre of the liquid bath, by which the heat is to be applied, and which may be water or oil, a solution of chloride of zinc, or, best of all, the fusible alloy of bismuth, tin, and lead. The capillary beak of the tube just projects over the surface of the bath, as in the figure. When the globe becomes sufficiently heated, the liquid boils, and its vapour, in passing away, carries off the air which had previously fill-



ed the globe. The liquid should be present in such quantity that its vapour, after carrying off all air, should occupy the interior of the globe completely pure. The excess of vapour is known to have passed away when there is no longer a jet proceeding from the capillary beak, and then by means of a blowpipe the orifice is closed, and the temperature of the bath being taken at the same moment, the globe is removed from the bath, perfectly cleaned and weighed. The liquid condensing as soon as the globe grows cold, leaves its interior practically empty, and, on breaking off the capillary beak under the surface of quicksilver, this last enters into the vessel, and, if the operation had been well managed, fills it completely. The globe, full of quicksilver, is then emptied into a graduated jar, by which the quantity of the quicksilver being measured, the volume of the globe is known; when this has been done, all requisites for calculating the specific gravity of the vapour have been obtained. For, knowing the volume of the globe, the weight of the air it contained is known, and, subtracting that from the first weighing of the globe, the weight of the globe *when empty* is obtained. Subtracting this from the second weighing of the globe, the weight of the vapour is obtained; and as the air and vapour occupied the same volume, the densities should be as these weights, if they had been at the same temperature; but, as this was not the case, a farther calculation is required to reduce them to the standard, and obtain the numerical specific gravities.

No process has been more fruitful in important results than this mode of determining the specific gravity of vapours, for it is only in this way that such substances as sulphur, arsenic, phosphorus, and mercury, as well as numerous compound bodies with high boiling points, could have been tried.

The force of gravity is thus of importance in chemistry, by giving a measure of the quantity of matter upon which we experiment, and by affording characteristics of individual substances, by the comparison of the quantity of matter they possess in a standard volume. The force of cohesion, although not so universally existant as that of gravity, is of equal interest, from the numerous peculiarities in its activity which almost everybody is capable of presenting, and by which bodies are remarkably distinguished from each other. To understand, however, the nature of cohesive forces, and the causes of the variation of their energy, it is necessary to notice those ideas of the peculiar constitution of matter on which philosophers have generally agreed, and which result from, while they best serve to explain, those remarkable phenomena.

From the earliest period in science, discussions have arisen as to whether the masses of matter which we ordinarily employ should be considered capable of infinite division, or whether, by continuing to divide, a term should ultimately be found at which no farther subdivision could be made; that thus the ultimate constituent and indivisible particles, or atoms, which, by their aggregation, form sensible masses, should be discovered. By no appeal to experiment can this question be resolved; when we call in the assistance of our most powerful means of mechanical division, we attain only to producing powders, of which the finest particle is, in miniature, all that the mass from which it had been formed was upon a larger scale, and capable evidently of just as much subdivision, if our mechanical processes were perfect enough to enable us to proceed.

That this divisibility may actually occur to an almost incredible degree, may be easily demonstrated by experiment. In gilding silver wire, a grain of gold is spread over a surface of 1400 square inches; and as, when examined in a microscope, the gold upon the thousandth of a linear inch, or one millionth of a square inch, is distinctly visible, it is proved that gold may be divided into particles of at least $\frac{1}{1\cdot400\cdot000\cdot000}$ of a square inch in size, and yet possess

the colour and all other characters of the largest mass. If a grain of copper be dissolved in nitric acid, and then in water of ammonia, it will give a decided violet colour to 392 cubic inches of water. Even supposing that each portion of the liquor of the size of a grain of sand, and of which there are a million in a cubic inch, contains only one particle of copper, the grain must have divided itself into 392 million parts. A single drop of a strong solution of indigo, wherein at least 500·000 distinctly visible portions can be shown, colours 1000 cubic inches of water; and as this mass of water contains certainly 500·000 times the bulk of the drop of indigo solution, the particles of the indigo must be smaller than $\frac{1}{2500\cdot000\cdot000\cdot000}$ the twenty-five hundred millionth of a cubic inch. A rather more distinct experiment is the following: if we dissolve a fragment of silver, of 0·01 of a cubic line in size, in nitric acid, it will render distinctly milky 500 cubic inches of a clear solution of common salt. Hence the magnitude of each particle of silver cannot exceed, but must rather fall far short of, a billionth of a cubic line. To render the idea of this degree of division more distinct than the mere mention of so imperfectly conceivable a number as a billion could effect, it may be added, that a man, to reckon with a watch, counting day and night, a single billion of seconds, would require 31·675 years.

In the organized kingdoms of nature even this excessive tenuity of matter is far surpassed. An Irish girl has spun linen yarn of which a pound was 1432 English miles in length, and of which, consequently, 17 lbs. 13 oz. would have girt the globe; a distinctly visible portion of such thread could not have weighed more than $\frac{1}{127\cdot085\cdot000}$ of a grain. Cotton has been spun so that a pound of thread was 203·000 yards in length, and wool 168·000 yards. And yet these, so far from being ultimate particles of matter, must have contained more than one vegetable or animal fibre; that fibre being itself of complex organization, and built up of an indefinitely great number of more simple forms of matter.

The microscope has, however, revealed to us still greater wonders as to the degree of minuteness which even complex bodies are capable of possessing. Each new improvement in our instruments displays to us new races of animals, too minute to be observed before, and of which it would require the heaping together of millions upon millions to be visible to the naked eye. And yet these animals live and feed, and have their organs for locomotion and prehension, their appetites to gratify, their dangers to avoid. They possess circulating systems often highly complex, and blood, with globules bearing to them, by analogy, the same proportion in size that our blood globules do to us; and yet these globules, themselves organized, possessed of definite structure, lead us merely to a point where all power of distinct conception ceases; where we discover that nothing is great or small but by comparison, and that presented by Nature on the one hand with magnitudes infinitely great, and on the other with as inconceivable minuteness, it only remains to bow down before the omnipotence of Nature's Lord, and own our inability to understand Him.

These proofs of great divisibility, however, leave the question of infinite divisibility quite untouched. There are, however, many and

powerful reasons which have decided almost all modern philosophers to consider the possible division as being finite. On the other view the mind has no resting-place, until, by the total disappearance of material conceptions, the constitution of bodies resolves itself into a collection of mathematical points, from which, as centres, certain forces are exerted; but with such abstract speculation chemistry has no connexion. Its fundamental condition, that there exist many kinds of elementary matter, of which the quantity is measured by their weight, is totally independent of our abstract idea of what matter is, or how its properties have their source.

In proof of the division of matter having a limit, experiments made principally by Faraday and Wollaston have been quoted. Thus, it is ascertained that our atmosphere does not extend into space, but is confined within comparatively a trifling distance from the earth, about 45 miles. Wollaston, considering the particles of air as being balanced between their mutual repulsion and the general attraction towards the earth, suggested that, if these particles could be divided to an infinite degree, there should be an infinite source of repulsive power, and hence, at a certain distance, this repulsion overcoming the gravitating force, the atmosphere should spread into space, and, being attracted to the other planets in proportion to their masses, should form round the larger, as Jupiter, and especially the Sun, vast and dense atmospheres, the existence of which should easily be recognised. No such atmospheres exist, and hence, as was argued by Wollaston, the force of repulsion must have a finite limit, and the number of repelling particles cannot be infinite. In like manner, Faraday found that bodies, in evaporating, form atmospheres of certain definite depths above the surface of the body, and drew from hence the same conclusion. This argument cannot, however, be considered as decisive. It is not at all certain that, because the elasticity of air is thus found to have a limit, the number of particles of air, in a given space, might not be infinite.

I shall consider the masses of matter, whose properties we purpose to examine, as being made up of a great number of lesser masses, to which the name of molecules or particles may be assigned. It is totally indifferent whether these molecules may be infinitely divisible or not; there is no fact in either chemistry or physics which requires the positive adoption of either one side or the other. These molecules are subjected to the influence of two forces, which oppose each other, and by the relative balancing or preponderance of which, all the forms and physical properties of ordinary substances are produced. One of these forces is attractive; it is the attraction of aggregation, as it has been termed, or cohesion. If it acted unimpeded, the molecules of every portion of matter would cohere with insuperable power; unconquerable solidity, hardness, and tenacity would alone characterize external nature. The other force is one of repulsion, which, from a variety of evidence, is assumed as identical with the cause of heat. If it alone prevailed, no other form of matter could exist but that of gas; the solid globe, the liquid waters, would change to atmospheres of vapours, and the beneficent uses to which our earth is now adapted could not exist.

Such is, perhaps, approximatively what occurs in those extreme

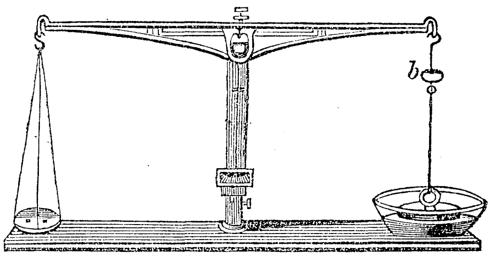
members of our planetary system, Herschel and Mercury. The former receiving from the Sun but $\frac{1}{400}$ part of the heat which our earth derives, must be reduced to the temperature of empty space; and, with few exceptions, the bodies which on this earth are gaseous or liquid, if they exist, are there as rocky masses. The latter must at certain periods be so hot, that quicksilver would naturally be a gas upon its surface, and those metals which here constitute our examples of solidity, should there form liquid oceans. On this earth, however, according as the forces of heat and cohesion vary in different bodies, they pass through different states of aggregation. Those bodies in which cohesion prevails are solid, and by their tenacity and resistance to breakage or change of form, display the force which binds their molecules together. Where cohesion has been suppressed, and the repulsive agency of heat acts uncontrolled, the body becomes gaseous, and its particles, devoid of the least trace of cohesive power, repel each other. In intermediate cases, where the two forces appear balanced, the particles do not cohere, and hence may move upon and separate from each other without any external force; but they do not repel, and thus remain in contact if no external force tends to disturb them. This is the liquid condition; it is that of water, of alcohol, of oil, while air and steam are gaseous, and iron, wood, and stone are instances of the solid form.

The peculiar nature of each body determines whether, under common circumstances, it shall have one or the other of these forms; but there are few bodies which are not capable of assuming all the three. This is artificially effected by diminishing or increasing the degree of heat, and thus by cooling a liquid, it may, by the cohesion becoming greater, be converted into a solid; or by increasing the heat to which a solid is subjected, it may be converted into a liquid, and from thence into a gas. One liquid, pure alcohol, has not yet been frozen; some solids, as charcoal, have not yet been melted: organized bodies are generally decomposed too easily to allow of a change of state; but, with these exceptions, the principle of the change of form, artificially caused by the increase or diminution of the quantity of heat, is universal. These forms of matter, considered as effects of heat, will require and obtain hereafter a more extended notice.

This force of molecular cohesion acts only at distances so minute as to escape the most delicate examination. The fragments of a piece of glass or metal which has been just broken, when laid ever so closely together, have no tendency to unite again; but, if the surfaces be pressed together, union may take place, though only in a few points, and imperfectly. Yet, when pieces of plate glass, laid flat on each other, and subjected to considerable pressure, are allowed so to remain for a certain time, they are found to grow together so completely, that thick masses may often be ground as if they had always formed a single piece. If two surfaces of lead be cut quite clean and bright, and forcibly pressed together, they unite also, and may require a force of eighty or one hundred pounds to effect their separation. In fluids, although the force of cohesion is very nearly absent, yet it is not entirely so; the viscidity of fluids depending upon the traces of it which remain. The globular form of a rain drop, or of a drop of any fluid allowed to fall from

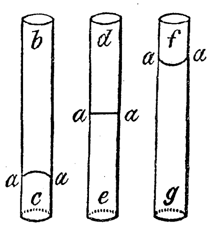
a point, arises also from the cohesive attraction of its particles, and different fluids differ remarkably in their relations to heat, from the various degrees of force with which this residue of cohesion is exerted. The particles of a fluid cohere not only to each other, but even more powerfully to solid bodies in many cases. It is thus that solid bodies are wetted by fluids. If the finger be dipped into water, the particles of the water in contact with the finger adhere to it more powerfully than they do to the other particles of the fluid, and when the finger is removed, they accompany it, and thus it becomes wet. Mercury does not wet the finger, for its particles cohere too powerfully to each other; but mercury adheres to, or wets a piece of gold, as water wets the finger. From this cohesion of fluids to solids, all the phenomena of capillary attraction result, as the filtering of liquids in pharmacy and chemistry, to separate solids which had been mixed with them; the absorption of liquids by porous solid bodies, and many others.

The existence of this form of cohesion may be very simply shown by an experiment, such as is illustrated in the figure. A disk of any substance which may be wetted by water is to be hung evenly from the extremity of the beam of the balance, and brought exactly into contact with the water in the cup below.



It will be found necessary to augment considerably the weights in the scale dish opposite, to separate them; and, when the disk has been torn away from the surface of the water, the force overcome will be found to have been, not that of the solid to the liquid, which was still more intense, but the cohesion of the liquid particles to each other; for the solid is found to be wetted by a layer of liquid particles which it had torn from the general mass of liquid underneath. If the experiment be tried with a disk of polished iron, and mercury as the fluid, there is no wetting, and the force measured is really the cohesion of the solid to the fluid.

[Clairaut found, as the result of his mathematical investigations, that all the phenomena of capillary tubes depend upon the relation of two forces: 1st, The cohesion of the particles of the fluid for each other; and, 2d, The attraction of the particles of the solid for those of the fluid. When a glass tube is dipped into different liquids: if the force of attraction of the glass is less than *half* the force of cohesion of the fluid, the fluid will be depressed, and not rise to its hydrostatic level; if it be equal to half, the fluid will come precisely to its level; and if it be more than half, the fluid will rise in the tube.



Connected with these conditions is the figure of the boundary surface of the fluid. If three glass tubes, *b c*, *d e*, *f g*, be placed in fluids which respectively are depressed, at the true level, or at

an elevation, it will be seen that in *b c* the surface *a a* of the fluid is convex, in *d e* it is plane, and in *f g* it is concave.]

The particles of a body being held at certain distances from each other by the balance of their attraction and repulsion: if, by the application of an external force, as pressure, they be brought nearer, so as to occupy a smaller volume, the body is said to be compressible. If, when the external force is removed, the body, by the mutual repulsion of its particles, regain its original volume, it is said to be *elastic;* if, on the contrary, it remains as when compressed, it is called *inelastic*. In nature there are few bodies perfectly elastic, and none which can be said to be perfectly inelastic. In solid bodies, when pressure produces a change of volume, some traces of it are permanent; but in liquids and in gases, the restoration to the original bulk appears to be complete.

The amount to which solid and liquid bodies may be compressed is very small, so much so that very delicate methods are necessary to determine it. Thus it requires a pressure of about 400 lbs. upon each square inch of the surface of water to diminish its volume by the $\frac{1}{1000}$ part. In gases, however, the repulsive force acting without interference, and the particles being at much greater distances from one another than in the liquid or solid form, the amount of compressibility becomes very much increased, and the law by which it is regulated extremely simple, being, that the volume of any gas varies inversely as the pressure upon it; that it is doubled if the pressure be diminished to one half, and reduced to one half if the pressure upon its surface be doubled. Thus, supposing a gas to measure 100 volumes under the pressure of 20 lbs.,

Then with pressures of	80	. 40	. 20	. 10	. 5 lbs.
The volume becomes	25	. 50	. 100	. 200	. 400.

The gases which are used in chemical operations are liable to constant changes of volume, from the alterations in the weight of the surrounding atmosphere, by which they are always pressed; and hence, before we can tell how much of a gas we really have obtained by any process, it is necessary to ascertain the amount of atmospheric pressure, and to allow for it. The pressure which the air exercises is measured by the barometer, in which a column of quicksilver balances the pressure of the air, and varies in height according as this changes; the height of this mercurial column being accurately measured by a scale applied to the tube of the barometer. In these countries, the height of the barometric column fluctuates between 28 and 31 inches, but the average height of a year is about 29·8 inches. For simplicity, a number very near this, 30 inches, is taken as the standard pressure; and whenever the specific gravity, or the volume of a gas is given, without particular remark, this standard height of the barometer is understood to be the pressure.

If, therefore, we have a gas at a different pressure, it is usual, and often necessary, to reduce its volume to what it should have been under the standard pressure, or, as it is generally termed, to correct for pressure: to do this, we use the rule given above for the change of volume with the pressure. Thus, if, in an analysis of morphia, we obtain 4·54 cubic inches of nitrogen gas when the barometer is at 28·5 inches, we say that, expressing the volume at 30 inches by V,

$$V \cdot 28{\cdot}5 : : 4{\cdot}54 : 30, \text{ or } V = \frac{28{\cdot}5}{}\times 4{\cdot}54 = 4{\cdot}313.$$

Knowing, then, the weight of 100 cubic inches of nitrogen gas at 30 inches, the weight of 4·313 is easily obtained.

In this manner, the corrections for pressure, alluded to in the description of the modes of taking the specific gravities of gases and of vapours, are introduced. Thus, in taking the specific gravity of steam by Gay Lussac's process (page 14), the vapour occupying but a portion of the tube, there remains a column of mercury, suppose 5 inches high: the pressure on the vapour is therefore only the difference between that and the external pressure, and if this be 30 inches, is (30—5)=25. Then the measured volume of the steam is to what it should be at the standard pressure, as 30 to 25.

In certain cases, of which atmospheric air may be taken as an example, this rule, of the volume being inversely as the pressure, holds exactly; but there are many other gases, in which, when the compression is very great, the particles appear to be brought within the sphere of their respective cohesive forces, and the volume diminishes more rapidly than it ought by the rule. Thus, if a tube full of air and a tube full of sulphurous acid gas be exposed to exactly the same pressure, the volumes will not diminish in the same degree when the pressure becomes high, but as follows:

The air as . . .	1000	853	559	314.
Sulphurous acid as	1000	851	554	301

In some other gases the same variation has been observed.

If such a gas be still more violently compressed, its particles may be brought so completely within the sphere of cohesive action, that this force comes into active play, and the body changes from the gaseous to the liquid form. Thus many gases have been liquefied by a degree of pressure which differs for each gas, and is at 32° Fahrenheit as follows:

Name of gas.	Atmospheres.	Pounds to the Inch.
Nitrous Oxide	44	660
Carbonic Acid	36	540
Muriatic Acid	24	360
Sulphuretted Hydrogen	15	225
Ammonia	5	75
Cyanogen	3	45
Sulphurous Acid	2	30

Other gases, such as oxygen, hydrogen, and nitrogen, have been subjected to a pressure of 800 atmospheres, not only without becoming liquid, but without even deviating from the rule which implies perfect elasticity, and hence without even approximating to the term at which they should abandon the gaseous state. Notwithstanding this, we cannot consider that there is any physical difference of constitution between those liquefiable and non-liquefiable gases, and hence the conclusion is, that, by a suitable increase of pressure, the molecules of all gases might be so brought into coherent approximation, and converted into liquids.

With regard to the means of applying such pressure, and actually obtaining those gases in the liquid form, it is necessary to consider the manner in which such gases are generated, and such methods will consequently be described in the history of those bodies.

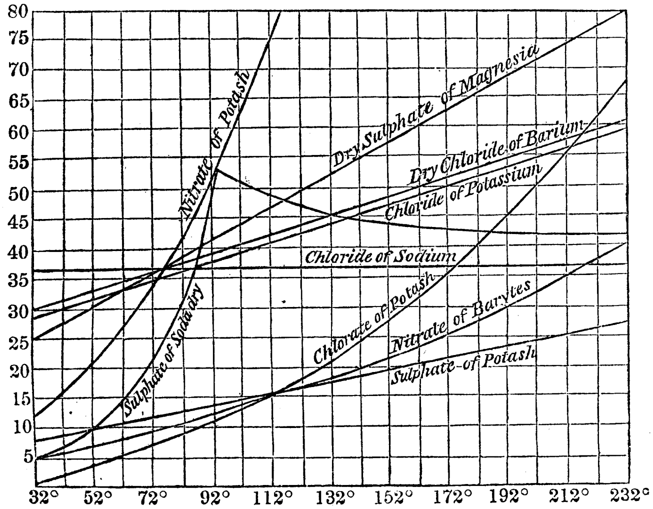
Cohesion is thus antagonistic to the force of heat, which tends to render the molecules of a body repulsive to each other, and to separate them to greater distances from each other than they had been

before. Cohesion is therefore diminished, and even annulled, by applying heat.

When the cohesion between the particles of a solid and those of a fluid is more powerful than between the particles of the solid itself, the latter is not merely moistened by the fluid, but it abandons altogether the solid form, and, becoming liquid, mixes uniformly with the fluid, and is said to have been dissolved by it. By this peculiarity of cohesion, bodies are divided into the *soluble* and the *insoluble*. Thus common salt and Glauber's salt are soluble, while chalk and white lead are insoluble, in water. These classes are, however, connected by a series of intermediate degrees of sparingly soluble bodies, such as cream of tartar and plaster of Paris. Bodies which are insoluble in water may be yet easily dissolved by other fluids; thus, resinous bodies, which do not dissolve in water, dissolve in alcohol. A great deal of the success of vegetable proximate analysis depends on the skill with which the solvent powers of various fluids may be successively applied.

From the tendency of heat to diminish the force of cohesion, it naturally results that the solubility of most bodies is increased by heat; thus, 100 parts of water, at 60° F., dissolve 11 of sulphate of potash, and at 212 dissolve 25. At 60°, 32 parts of dry sulphate of magnesia are dissolved by 100 of water, but 74 at 212°. This, however, is not always the case; some bodies, as common salt, are exactly equally soluble in water at all temperatures, while in other cases the solubility is greater at particular temperatures than either above or below them. Of this peculiarity, the sulphate and nitrate of soda are examples. Thus, 100 parts of water dissolve of dry sulphate of soda, at 32°, 5·02; at 52°, 10·22; at 76°, 28; at 93°, 53; at 122°, 47; and at 212°, 42: the solubility increasing up to 93°, and from thence diminishing. 100 parts of water dissolve of nitrate of soda, at 21°, 63; at 32°, 80; at 50°, 23; 60°, 55; and at 246°, 218 parts. Here the peculiarity is of the opposite kind to what occurs with sulphate of soda: the solubility diminishing up to 50°, and from thence progressively increasing.

The solubility of bodies in water may be strikingly represented to the eye by means of a kind of map, such as is given in the figure. The horizontal lines represent the quantities of the salt dissolved by 100 parts of water, while the vertical lines represent the temperatures. Thus the line of sulphate of soda commences



at the temperature of 32° at the horizontal line 5, and, rising rapidly, cuts the horizontal line 10 at 52°, cuts the line of 40 at 88°, and attains its highest point of 53 at 93°; from thence it commences to redescend, until at 232° there are only 42 parts dissolved. The line of chloride of sodium is horizontal, showing that it is equally soluble at all temperatures, and in the other cases the construction of the scale is easily seen on inspection.

In general, when solid bodies dissolve in a fluid, there is cold produced, but occasionally the solution is accompanied with a remarkable evolution of heat; this last occurs when bodies which naturally contain water, chemically combined, are deprived of it by heat, and when thus dried, dissolved; in such cases, it is probable that the one portion of water is taken by the salt into a state of intimate chemical combination, and thus more heat produced than counteracts the cold which should arise from the mere solution of the hydrated salt thus formed. Such examples may be found in dry chloride of calcium, the dry sulphates of copper, or of zinc and iron.

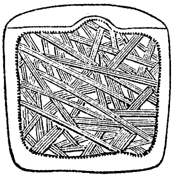
Solution is very much promoted by agitation, by the minute division of the solid, and generally by all causes which tend to facilitate the contact of the solid and liquid particles. When the liquid has dissolved as much of the solid as possible, it is said to be *saturated*. The cohesion of the liquid to the solid having been reduced to an equality with that of the particles of the solid for each other, it can dissolve no more.

If a saturated solution be so circumstanced as to diminish the cohesion of the particles of the solid to each other, a portion of the solid separates, the amount of which depends on the new conditions under which the liquid is placed. Thus, if to a solution of nitre in water there be added spirits of wine, the water mixes with the spirits of wine and abandons the nitre, which is precipitated If strong muriatic acid be added to a solution of chloride of barium in water, the water is taken by the acid, and the salt falls down as a white powder. But the most usual case is where the separation of the solid is produced by the cohesion of its own particles, which, slowly abandoning the liquid, dispose themselves according to certain laws, and, assuming regular geometrical forms, are termed *crystals*. Solid bodies, in separating slowly from liquids in which they had been dissolved, in general thus *crystallize*, and the figures of these crystals being, to a great extent, characteristic of the bodies, deserve minute attention.

To obtain substances regularly crystallized, several processes may be followed, according to the nature of the body. Where the substance is soluble, and more soluble in a hot than in a cold liquid, a saturated boiling solution may be made and allowed to cool. The excess of the solid body crystallizes out on cooling. Thus, if 151 parts of sulphate of magnesia in crystals be dissolved in 100 parts of boiling water, and allowed to cool to 60°, a quantity of crystals will be obtained weighing 86 parts; for at 60° the 100 of water can only dissolve 65, and the difference between that and the 151, which had been dissolved by the boiling water, must crystallize. If the body be, like common salt, equally soluble in water at all temperatures, the above process cannot be applied, and a quantity of the liquid must be removed by evaporation; the portion of salt corresponding to the quantity of water which has passed away, is thus obtained solid. If the evaporation be slowly carried on, so that the formation of the crystals is not disturbed by the boiling of the liquid, they form regularly, and may attain to considerable size.

In many cases the bodies which it is necessary to obtain crys-

tallized are not soluble, or it may be wished to obtain crystals otherwise than by solution. By melting a solid substance, its particles are allowed liberty of motion; and when it again commences to solidify, they may arrange themselves regularly, and crystallize. Almost all bodies, when melted, and then allowed to solidify, do thus crystallize; but the spaces left between the crystals which first form being completely filled up by the portions which solidify afterward, there remains only a general crystalline structure, visible in the fracture of the body. Thus cast iron, sulphur, zinc, &c., have crystalline fractures. The beautiful feathered appearance given to sheet tin by washing with dilute acid, and which was so popular some years ago under the name of *moirée metallique*, was simply this crystalline structure, displayed by removing the thin layer of metal on the outside, which had solidified too rapidly to have acquired any trace of crystallization. To obtain, therefore, the metals crystallized by fusion, the excess of liquid metal must be removed from around the crystals that are first formed. A quantity of the metal or of sulphur, having been melted in a cup, is to be allowed to cool until a solid crust has formed upon the surface and at the sides to a certain depth; two apertures must then be made in the upper crust, and the fluid metal remaining be poured out at the one aperture, while the air enters at the other to supply its place. On then breaking the vessel, the interior of the solid layer of metal or sulphur is generally found lined with well-formed and characteristic crystals, as represented in the figure.



Bodies may also be crystallized by sublimation. When a substance has been converted into vapour, and that, in condensing, it assumes at once the solid form, its particles arrange themselves so as to form crystals. Thus are obtained in fine crystals, arsenic, arsenious acid, corrosive sublimate, benzoic acid, &c.

It frequently happens that the same body may be obtained crystallized by more than one of these processes. Thus, corrosive sublimate may be crystallized by solution or by sublimation; sulphur may be crystallized either by fusion or by solution. It is remarkable that, when this occurs, the crystals obtained by the two processes are never of the same shape; they have not even any simple relation of figure to one another, but indicate a totally different mode of arrangement of particles, induced probably, at least in part, by the different temperatures at which the change of state of aggregation may have occurred. A body which crystallizes thus in two ways is said to be *dimorphous*, and this character will be found hereafter of the highest importance in the theory of the atomic constitution of compound bodies.

The more slowly the change of state occurs, the more regular, and the larger, are the crystals that are formed. Hence, in practice, solutions are left to cool very slowly, or to evaporate spontaneously; and sublimation is effected by the most gentle heat that can be advantageously applied. To favour the deposition of the particles, a variety of artificial aeids may be applied. Thus, crystallization takes place better in a pan with some little roughness at the sides

than when it is quite smooth, and threads are hung in sirup to promote the crystallization of the sugar-candy; a little crystal of the same kind of salt is often introduced, to serve as a nucleus round which the new crystals may gather; and, in a solution containing many salts, the nature of the salt which shall crystallize may be determined by the nature of the little crystal introduced: thus, if equal parts of nitre and of Glauber's salt be mixed and dissolved in five parts of water, and the solution divided between two similar dishes; on a crystal of nitre being laid in one dish and a crystal of Glauber's salt being laid in the other, a crystallization of pure nitre will occur in the former, while nothing but Glauber's salt will crystallize in the latter dish. Salts which are mixed together in solution may also be separated from one another by their respective solubilities: thus, if sea-water be evaporated, common salt alone will be deposited according as the liquor boils away; when it has been removed from the fire no more common salt separates, but Epsom salt will crystallize, and, after it has been removed, the liquor will be found to contain chloride and iodide of magnesium. The liquor from which crystals have separated is called the Mother liquor.

Crystals occasionally form in a body, although it may remain completely solid. Thus, when copper wire has been kept some time in the laboratory, it becomes a mass of cubical crystals, and its tenacity is almost completely lost. When sugar is melted and allowed to cool, it forms a perfectly transparent hard mass, destitute of any trace of crystalline arrangement, but after some months it becomes opaque and white, having changed into ordinary crystallized sugar. In cases, also, where bodies are dimorphous, one form is generally unstable, and the body, when crystallized in it, changes after some time into the other form. This takes place remarkably with sulphur, and will hereafter be again referred to.

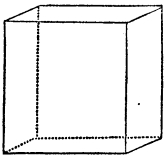
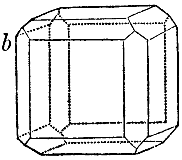
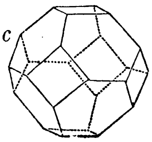
A solution of a salt, saturated at a high temperature, is found occasionally to remain without crystallizing, although cooled to a very low degree. In such case, on introducing a little crystal, or agitating the liquor, it suddenly crystallizes, and frequently solidifies into one mass. Sulphate of soda is remarkable for its tendency to assume this indifference to crystallization. If two parts of crystallized sulphate of soda be dissolved in one part of water, at 93°, and the solution be laid aside to cool, without being disturbed, it remains quite clear and liquid; but, on producing crystallization by any of the means just stated, the whole becomes solid.

In all cases of crystallization there is heat evolved, consequent on the general law of heat being given out when a liquid or vapour becomes solid. There is sometimes a remarkable evolution of light, to which I shall refer again. Indeed, crystallization is sensibly affected by the presence or absence of light. If a dish, half covered by paper, be set aside with a solution to crystallize, but few crystals will form in the dark, although there may be an abundant crop on the illuminated portion of the vessel.

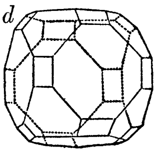
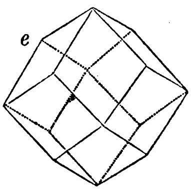
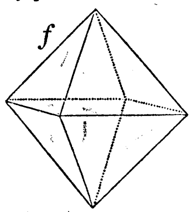
It has been noticed, that when a body has been obtained, crystallized at different temperatures, as by solution and fusion, the crystalline form is generally different, and the body is said to be

dimorphous. In this case, the two forms are totally different in their geometrical character. But independent of this, a body may, even simply by solution, be obtained, crystallized in a great variety of forms. In a crop of crystals of sulphate of iron or of alum, obtained by cooling from a hot solution, a great many different figures may be observed, which, however, are, on examination, all referrible to one more regular and fundamental form. Each substance has thus a characteristic form of crystal, which is termed its primary form; and it may assume a great variety of figures, produced by modifications of this form: these are termed secondary forms. Thus, carbonate of lime has been found crystallized in more than six hundred different secondary forms, all derivable, however, from the one original primary figure, the rhombohedron. The growth of a crystal depending on the deposition of new layers of particles over its external surface, any change in the quantity deposited on each side will naturally produce a change of form. It is therefore necessary, when crystals are left long in a solution, to turn them, and change their position frequently, as otherwise the growth would take place on some sides rather than others, and secondary forms would be produced, by which the characteristic figure of the crystal would be injured.

The most ordinary source of change of figure consists in the replacement of an edge or of an angle by a plane. Thus one of the simplest figures of crystals is the cube *a*; it has eight edges and eight solid angles. The effect of substituting plane surfaces for the edges is to produce the secondary form *b*, and by replacing the solid angles by planes, the form *c*; when these replacements occur together,

a

b

c


the more complex figure *d* is produced. If the edges of the cube be replaced until all traces of the original planes disappear, the figure *e*, the rhombic dodecahedron, is produced; and if the replacement of the solid angles by planes be carried on to

d

e

f


the same extent, there is formed a regular octohedron *f*. These last are again simple and primary forms, for by a similar move of replacement they may be reduced to each other or to the cube.

When a crystal augments in size by the deposition of layers of fresh material upon its faces, the molecular cohesion in each new layer is greater than its cohesion to the layer underneath, and hence, by skilful splitting, a crystal may be separated into a number of plates, exhibiting the order of its formation. The direction in which a crystal may be split is termed its cleavage, and it is of great importance in the determination of the primary form of the crys-

tal, for it often occurs that the same secondary form may be produced by two different primary forms, and in such case, the cleavage being simply related to the surfaces of the true primary form, determines which it is.

Notwithstanding the immense variety of forms of crystals which exist, they may yet be reduced to a very few classes, by conceiving them to be formed by their particles being built up around certain axes, which pass through the centre of the crystal, and the relative position and magnitude of which determine the manner in which the particles are arranged.

In this way there may be formed six systems of crystallization, characterized as follows:

1st System. *The Regular System.* The three axes are all equal in length, and are at right angles to each other.

2d System. *The Rhombohedral System* has three axes equal in length, which are placed, however, at equal angles (60°) with each other, and are all in the same plane, while a fourth and unequal axis is at right angles to that plane.

3d System. *The Square Prismatic System* has the three axes at right angles to each other, but there are only two of them equal; the third is either longer or shorter than the other two.

4th System. *The Right Prismatic System* has the three axes at right angles to each other, but there are no two of them of the same length.

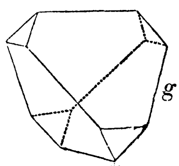
5th System. *The Oblique Prismatic System* has two of the axes making an acute angle with each other, while the third is placed at right angles to both. The three axes are all unequal in length.

6th System. *The Doubly Oblique Prismatic System* has all the axes unequal in length, and making acute angles with one another.

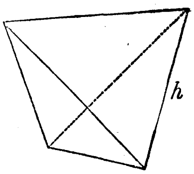
The various actual forms of crystals, both primary and secondary, are derivable from the manner in which the plane surfaces of the crystals may be applied around these axes. In order to conceive the application of the planes, the axes shall be considered as placed with one in a vertical position, and it is called the principal axis. The nature of the system determines which axis should be selected.

In the *Regular System*, the axes being all equal, it is a matter of indifference which is chosen as the principal axis, and their perfect symmetry is also a reason that the portions of the crystal around each axis must be completely similar. The number of forms belonging to this system is consequently not very large, and they are remarkable for their simplicity. Thus, when each plane cuts the axes at equal distances from the centre, the form is the octohedron, and as the planes must be equally inclined to all the axes, it is the regular octohedron *f*, of which each plane is an equilateral triangle. When each face of the crystal cuts one axis at right angles, and is hence parallel to the other two, the form is the cube *a*. When each face cuts two axes at equal distances from the centre, and is parallel to the third, the figure which results is the rhombic dodecahedron *e*. By the combined positions of sets of planes, other and more complicated (secondary) *b*, *c*, *d*, forms are produced, arising from the partial coexistence of the conditions of the formation of two simple forms.

The crystals belonging to this system are generally very well defined and easily recognised: a great number of important bodies crystallize in the forms belonging to it: thus common salt, fluor spar, galena, and iron pyrites, are found in cubes; alum in octohedrons; the garnet is found in dodecahedrons. When pure metallic substances are found crystallized, it is always in forms belonging to this system; thus, bismuth, copper, silver, gold, crystallize in cubes, and lead in octohedrons.

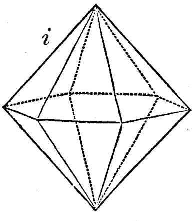

g

A peculiarity of crystals, belonging particularly to this system and to the next, is, that every alternate face shall become developed to such a degree as to obliterate the intervening planes, and thus to generate a new form, having one half of the number of planes. Thus a crystal of alum is very seldom truly octohedral; it has usually the figure of *g* where four of the sides of the octohedron have become very large, while the other four remain very small. When the obliteration becomes complete, there is produced the tetrahedron, or three-sided pyramid of fig. *h*, which is hence properly called

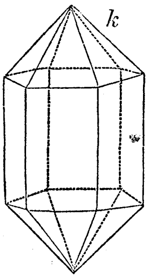

h

the hemioctohedron. Such crystals are called hemihedral, from their containing half the proper number of sides. Certain bodies have a natural tendency to hemihedral crystallization, and are but very rarely found with the proper number of planes. The diamond is a remarkable instance of this. Its proper form is the regular octohedron, but its crystals are universally hemihedral.

i

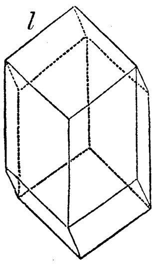


k

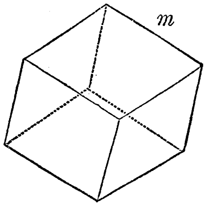


In the *Rhombohedral* system, the supplementary, or fourth axis, is taken as the principal axis, and the crystals are formed by the planes being applied to these axes, as in the former system. If the planes be all inclined at the same angles to the three horizontal axes, and cut the vertical axis, there is formed a double six-sided pyramid (*i*); and when the planes are perpendicular to the horizontal axes, and parallel to the vertical axis, the six-sided prism (*k*) is produced. These forms generally coexist in quartz, as in the figure *k*. By the replacement of the edges in these forms there may be produced others with twelve sides in place of six; as a twelve-sided prism and a twelve-sided pyramid, of which quartz also affords examples.

l



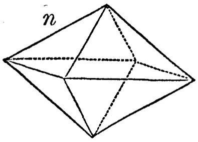
m



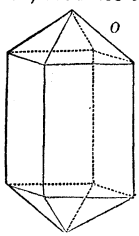
This system is more remarkable for its modified forms than for those simple figures above described, although the six-sided prism and six-sided pyramid are characteristic of very many substances. If we suppose, in the terminal six-sided pyramid, every alternate side, above and below, to grow at the expense of those next it at each side, *l* will be formed. Ultimately the sides of the prism disappear, and there will remain a figure of six planes, of which all the sides shall be equal and similar rhombs, the rhombohedron, *m*, which gives its name to this system, although it be but a hemihedral modification of the true typical form. The principal axis of the rhombohedron is the vertical axis of the pyramid, and the horizontal axes are found by joining the solid angles to the centres of the opposite faces, where originally the lateral angles of the pyramid had been.

The carbonates of lime, of iron, and magnesia are remarkable for crystallizing with this hemihedral figure. Even in the six-sided prism of carbonate of lime, the rhombohedral tendency is evident by the crystal being terminated, not by the six-sided prism, as in quartz, but by its three hemihedral replacing planes.

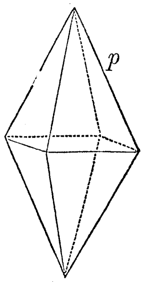
n



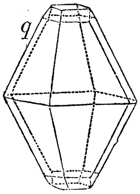
o



3. *The Square Prismatic System.*—The crystals of this class differ from those of the regular system in the vertical axis not being necessarily equal to the other two; but, on the contrary, being in almost all cases either longer or shorter. Where there is formed an octohedron, *n*, it differs from the regular octohedron in the terminal angle of each plane being not 60°, but more or less. Its basis is, however, a square; and to distinguish it from the octohedron of the following system, it is termed the octohedron with the square base. By the application of planes perpendicular to the horizontal axes, a four-sided pyramid with a square base is formed, *o*, and by the replacement of the terminal edges of this prism, four-sided pyramids may be formed on its base and summit. By this property the square prisms and octohedrons are distinguished from all modifications of the cube and octohedron of the regular system. When the edge of a cube is replaced, the plane substituted for it gains equally on the two surfaces, and hence, when one is effaced, the other must be so also. But in the square prisms the replacement may efface the terminal plane, giving a four-sided pyramid, and yet the lateral planes be but little encroached upon. The sides of the crystal in this system are thus independent of the top or bottom, and may be modified, while the top and bottom remain unaltered; this never takes place in the regular system, where, there being no one side particularly upper or lower, all modifications must affect all sides alike.

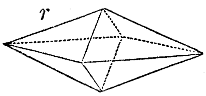


4. *The right Prismatic System.*—In this system the three axes being all unequal, the length, breadth, and thickness of the crystal may be different from each other. Thus, in the octohedron, *p*, formed by the application of planes, each connecting the extremities of the three axes, the three dimensions of the crystal, as in the figure, which is the primitive form of sulphur, are unequal; the octohedron has a rhombic base; and by planes which are inclined to the horizontal axes, and parallel to the vertical axis, a prism with a rhombic base may be produced. This also, by combination of the two forms, may obtain pyramidal terminations, as in some forms of native sulphur.

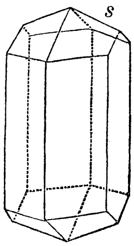


An important character of this system, which arises from there being no necessary connexion between the two horizontal axes, is, that the lateral edges may be alternately modified in a different manner; or, in other words, that, looking at the crystal, its back and front may be differently affected from its sides. Of this an example may be found in a common modification of the sulphur octohedron given in figure *q*.

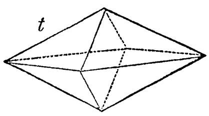
5. *The oblique Prismatic System.*—From the manner in which the crystals belonging to this system form, one of the oblique axes is generally by much the most developed, and is taken as the principal axis. The remaining axes, which are at right angles to each other, are taken as horizontal, the principal axis making with them the acute angle, which belongs to the peculiar body.



By means of planes which are inclined to all the axes, there is formed the oblique rhombic octohedron, such as characterizes gypsum (sulphate of lime), as in figure *r;* and by means of planes which are inclined to two axes, but parallel to the third, an oblique rhombic prism may be formed, *s*. A remarkable character of these crystals is, that from the crossing of the axes and their independence of each other, the front and back of the crystal may be quite different in relation to the sides. The crystals of sulphate of soda, of carbonate of soda, of borax, of sulphate of iron, and of feldspar, may be taken as examples of the numerous forms derivable from this system.



6. *The doubly oblique Prismatic System.*—The axes are all unequal, and all form acute angles with each other, and it is hence indifferent which is taken as the principal axis of the crystal. The consequence is complete absence of symmetry between any two surfaces of the crystal, except such as, being at the ends of the same axis, are parallel to each other.



The complexity of crystals of this system is hence usually very great. The simplest forms are the oblique rhombic octohedron, *t*, and the oblique rhombic prism, formed by planes inclined to all the axes, or to two, and parallel to the third, respectively. The soda feldspar (albit) and sulphur of copper are examples of this system; the octohedron of this system is figured in the margin.

It might be at first supposed that the assumption of these axes, or lines round which we have supposed the crystalline particles to be regularly arranged, was merely a geometrical fiction, by which the form of the crystal might be more easily represented to the mind; but such is not the case. Evidence derived from a variety of sources agrees in demonstrating that this diversity of crystalline systems arises from fundamental differences in the laws of molecular cohesion, by which the formation of the crystal is regulated, and that these axes, which have been so much alluded to, are real centres, the proportion and position of which determine all the physical properties of the body. It is peculiarly from the action of crystallized bodies upon light that accurate and extraordinary information has been obtained of their internal structure, and the discoveries that have been made in this department were the means of advancing the physical theory of light to its present almost perfect state.

Substances may assume crystalline forms which do not properly belong to them in many ways. Thus, a group of crystals being imbedded in a rock, they may, by the filtration of the water of springs across the rock, be dissolved out, leaving a hol-

low mould of their form; and, subsequently, substances of another kind may be introduced into this cavity, and, solidifying there, may simulate the external form of the original inhabitant. But these are no more real crystals than a mass of plaster of Paris, which has solidified in a hollow mould, and comes out as an Apollo's head, can be said to have so crystallized. By cleavage, and by the operation of polarized light, the unsuited internal structure is recognised, and the crystal is stated to have been merely *pseudomorphous*. Another mode in which a body may come to have a form not its own, is by remaining behind after the decomposition of the substance which had really crystallized. Thus, when hydrated chloride of copper, which crystallizes in fine green prisms, is carefully heated, the water is expelled, and the chloride of copper remains dry, and of a fine yellowish-brown colour, in the original crystalline form, and with the surfaces quite bright. The red iodide of mercury combines with ammonia to form a substance which crystallizes in long prisms of a snow-white colour; these, when exposed to the air, lose all ammonia, and the iodide of mercury remains behind, pure, and of a brilliant red, but with the perfect figure, and bright, smooth surfaces and sharp angles of the body originally crystallized.

It has been thought that the presence of foreign bodies in a solution, even where they did not enter into combination with the substances which crystallized from it, might modify their form. Thus, when common salt crystallizes in a solution of urea, it is deposited in octohedrons, and by dissolving alum in a solution of urea, it may be obtained crystallized in cubes. But in this case, the substances which crystallize are no longer common salt nor alum, but the one, a combination of urea with common salt, and the other, a basic alum produced by the mutual decomposition of the urea and the alum. The presence of a trace of lead or tin in a large quantity of iodide of potassium, has been supposed to modify its form; but it is more likely that the mechanical presence of an impurity of the kind may be supposed to produce a tendency to macled crystals, and thus the external form be somewhat altered, although the true constitution of the crystal may remain the same.

Certain bodies, when they exist together in solution, may remarkably modify each other's form, by crystallizing together so completely that every individual crystal shall contain a quantity of each. Yet these bodies will not have combined chemically with each other, for the quantity of each present in each crystal is quite indefinite; they are mixed together mechanically in the crystals, and hence the form of the actual crystal is intermediate between those which the separate bodies should have had if they were pure. In order that bodies may so crystallize together, it is not only necessary that they should be of the same crystalline system, but the crystalline forms must resemble one another very closely in all their angles and sides. Thus, not only will iodide of potassium and sulphate of soda, which belong to different systems of crystallization, not crystallize together, but Glauber salt and carbonate of soda, which do belong to the same system, will not crystallize together, because the relations of their angles and sides being completely different, they cannot mix together so as to form a uniform solid. But sulphate of zinc and sulphate of magnesia belong not merely to the same crystalline system, but they are almost identical in their figures; the eye cannot make any distinction between their crystals; and hence, when a crystal is being formed in a solution containing these two bodies, the molecular and crystalline forces being the same for both, they concur in the building of the crystal without interfering with each other. Hence, as there is a very small difference between the angles of the rhombic prisms of the two salts, the one being 90° 30′, and the other 91° 8′, if they be mixed in equal proportions in the crystal, its angle must be 90° 49′. Carbonate of lime and carbonate of magnesia are, like the

sulphates of zinc and magnesia, almost identical in crystalline form, and they exist in nature mixed together, forming the dolomite or magnesian limestone. The quantity of carbonate of lime is to the quantity of carbonate of magnesia as 50·6 to 42·8; and as the angle of the rhomb of carbonate of lime is 105° 4′, and that of carbonate of magnesia is 107° 40′, the angle of the mixed crystal is found by multiplying the angle of each constituent by its quantity, adding these products together, and dividing by the quantity of the mixture, and the result is 106° 15′, the angle of the rhombic crystal of magnesian limestone.

The peculiarity of crystallization which such bodies possess may be illustrated in another manner. Ordinary alum is a sulphate of alumina and potash; but there are a great variety of other double sulphates which crystallize in the same form, and which constitute a well-defined crystalline genus. If an octohedral crystal of common alum be placed in a solution of the sulphate of alumina and ammonia, the crystal augments in size by the addition of layers of it. If it be then removed to a solution of sulphate of potash and peroxide of iron, it acquires another layer; by a solution of sulphate of ammonia and peroxide of iron another still; and by means of solutions of the alums, which consist of oxide of chrome united to potash or ammonia, with sulphuric acid, the crystal may grow to a still greater size. The chemical constituents of the crystal may thus vary, but it retains its form; the number of equivalents of chemical substances contained in it remains also the same, although they may not remain identical in nature. The potash and the ammonia on the one hand, the oxide of iron, the alumina, and the oxide of chrome on the other, agree in producing the same crystalline arrangement of particles; in impressing upon their compounds, with the same bodies, the same crystalline form. Bodies so related are called *isomorphous*. Oxide of zinc and magnesia are isomorphous; while lime is a dimorphous body, being in one form isomorphous with magnesia, and in the other with oxide of lead. *Isomorphous* bodies are remarkably similar in their chemical properties; they follow generally the same laws of combination, and hence, as shall be farther shown in the chapter on chemical affinity, the principle of *isomorphism* has been of the highest importance in developing the true relations of chemical substances to each other, and the intimate connexion of the forces which produce the chemical combination, and those which direct the crystalline arrangement of the particles of bodies.

It was, some time ago, considered an important question, whether the ultimate particles of bodies had the same figure as their primary crystalline form, or whether they were globular or ellipsoidal. The law of isomorphism was considered, at one time, to result from the ultimate particles of those bodies, being themselves isomorphous; and hence, when entering into similar combinations, giving to them also the same form. It was at another time referred to the principle that, in any chemical combination, the crystalline form was determined by the number of molecules or atoms present, and was independent of their nature. Neither of these ideas has been found sufficient; but the complete discussion of the relations of the isomorphous bodies will be found in a future chapter.

The angular dimensions of crystals being thus the measures by which they are recognised and compared with one another, the instruments by means of which their measurement is effected re-

quire a few words' notice. They are called goniometers (γονιος, an angle; μετρω, I measure). The simplest form consists of a semicircular scale of degrees attached to a pair of blades, which, crossing each other at the centre, allow of the crystal being adjusted exactly to their edges, and then show the value of the angle by the number of degrees intercepted on the scale between the blades. For all purposes requiring accuracy, the goniometer of Wollaston must be applied. In it, the angle of the crystal is determined by measuring the number of degrees through which it is necessary to turn the crystal in order that two rays of light, reflected successively from the two surfaces, including the angle, may be in exactly the same direction. To the adoption of this principle of measurement we owe almost all the great advance that has been lately made in the relations of the crystalline forms of bodies to their chemical and molecular constitution.

In all that has formed the subject of the chapter which has now closed, the forces brought into play, and the effects which were produced by means of their action, were not such as to involve the principle upon which all purely chemical phenomena are based, the existence of a variety of elements. The laws of cohesion, from its simplest action in a liquid to its most complex manifestation in a double oblique crystal, might have existed in nature, and, being studied, make a part of science, independent of any consideration of true chemical force, although serving most usefully for the identification of chemical substances, and capable of modifying the circumstances of their mutual action in an eminent degree.

CHAPTER II.

OF THE PROPERTIES OF LIGHT AS CHARACTERIZING CHEMICAL SUBSTANCES

I SHALL not attempt to enter into the details of the history of the mechanical properties of light, as they constitute one of the most purely mathematical of the physical sciences, and have but indirectly a relation to chemical phenomena: a short notice of these properties is, however, necessary, in order that the means of recognising chemical substances may be fully given.

Light, emanating from any luminous body, moves in straight lines; the smallest portion of it which can be admitted through an aperture being termed a ray. When a ray of light falls upon the surface of a body, it is either bent back again, or it passes into the substance of the body; the bending back is termed *reflection*, and is regulated by the law, that the angles of incidence upon the surface, and of reflection from it, are always equal. It is thus that the images are formed in a looking-glass; for we see objects in the direction in which the ray of light arrives at the eye, and hence we judge the image to be as much behind the mirror as the object is before it.

When the ray of light has passed into the substance of the body,

it may be *absorbed*, in which case the substance, not sending any light to the eye, appears completely black, or is, rather, totally invisible, except by contrast with some other body placed behind it; or the light may be transmitted, in which case the body is said to be *transparent*, as the light may arrive at the eye after passing through the substance. Bodies which do not transmit light are said to be *opaque;* but there are two kinds of opacity, that of blackness, where the light which falls upon the object is totally lost by being absorbed, and that of whiteness, where the light is reflected, and we can see the object itself, though we cannot see anything through it. Where, in an opaque body, the light is partly reflected to the eye and partly absorbed, there arises the diversity of colours which opaque bodies may possess.

When the ray of light is neither totally reflected from the surface nor lost within the substance of the body, but passes through it, it is *refracted;* that is, its direction is changed; and if its path be represented by a line, it is broken at the surface of the medium, and hence the name. It is thus that an oar, partly immersed in water, appears broken at the surface. Any substance through which light is moving is termed a *medium*, and the refraction occurs at the limiting surface of the two media, as air and water, air and glass, though not to the same degree as if the light had passed into the most refractive medium directly from an empty space. This refractive power is of importance as a characteristic property of bodies, but to the chemist it is specially of use in the study of crystallized bodies; and it is hence with reference to the principles of the molecular structure of those substances already noticed, that the refraction of white light shall be examined.

This reflection, absorption, or transmission of the luminous rays which fall upon the surface of a body is, however, in no case absolute and simple. All bodies reflect some light, and there are none which allow light to pass through them without its undergoing some absorption. In general, light incident upon a body is divided into three unequal parts, of which one is reflected, another absorbed, and the third transmitted, and the nature of the body determines which action shall be most powerful.

In uncrystallized bodies, a ray of light, in passing from a rarer to a denser medium, is generally bent towards a line perpendicular to the surface of the medium, and in passing from a denser to a rarer medium, the refraction is from the perpendicular. In this case, the law of refraction is such that the sines of the angles of incidence and refraction are to each other in a constant proportion, no matter how the direction of the incident ray may change, and the number which expresses this ratio is called the index of refraction.

The velocity with which light is transmitted is exceedingly great; the light of the sun arrives at the earth in eight minutes, being at the rate of 195,000 miles in a second. This, however, is but the mean velocity of the coloured lights which a solar ray contains, for these differ in velocity, those which are least refrangible being transmitted with the greatest quickness. The velocity of light is changed when it passes from one substance to another, and it is this change in which originates refraction. In general, the denser the medium

the more is the velocity diminished; and it was by the experimental proof of this that one of the most triumphant testimonies in favour of the undulatory theory of light was found.

The refractive power of a body is not connected with its chemical constitution in any positive manner; but inflammable substances are generally possessed of high refractive powers. It was this which led Newton to the celebrated prophecy that the diamond should be combustible, and that water should possess an inflammable constituent; but many bodies of high refracting powers are not at all combustible.

The refracting power, as measured by the refractive index, is given for some of the more remarkable bodies in the following table:

Realgar	2·549	Garnet	1·815
Octohedrite	2·500	Oil of cassia	1·614
Diamond	2·439	Plate glass	1·542
Nitrate of lead	2·322	Oil of turpentine	1·475
Phosphorus	2·224	Water	1·336
Sulphur	2·148	Chlorine	1·000772
Flint glass, from	2·028	Air	1·000294
to	1·830	Vacuum	1·000000

In uncrystallized bodies, the molecular arrangement being irregular and indefinite, the action upon light is the same in every direction, and hence a ray of light undergoes, when passing from air into water or glass, simple ordinary refraction; it is bent out of its path by an angle which depends upon the angle of incidence, by the law of the proportionality of their sines. In bodies which crystallize in the regular system, where there are three precisely similar axes, the molecular constitution, although subjected to definite laws, must be the same in all directions, and hence a ray of light will be acted upon, in such a crystal, in the same manner, no matter in what direction it may go. Hence, in crystals of the regular system, there is only ordinary refraction and a single image.

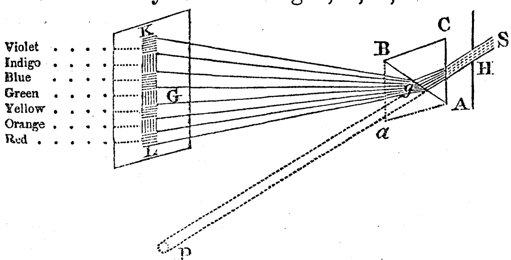
When a ray of light passes, however, into a crystal of the rhombohedral system, it is differently acted upon, according to the part of the crystal it passes through. If it pass along the principal axis, it is equally related on all sides to the crystalline forces, and hence, as in the crystals of the regular system, there is only a single refracted ray. But if the light pass in any other direction, it is divided into two portions, one of which is refracted according to the ordinary law of the sines, while the other, following a totally new law, is termed the extraordinary ray. The angle which these two rays make with each other increases according as the path of the incident ray is farther from the principal axis; and when the light falls perpendicular to the sides of the prism, and hence to the principal axis, the divergence of the two refracted rays is the greatest possible. In the square prismatic system, the same peculiar action upon light exists; when a ray of light passes along the principal axis of the crystal, it undergoes simple refraction according to the ordinary law, but in any other direction the ray is subdivided into two, of which one is refracted in the ordinary way, and the other follows a new and peculiar law.

The existence of double refraction, and the change in its amount, according to the direction in which the light passes through the

crystal, may easily be observed. If a round dot be marked with ink on a sheet of paper, and a rhomb of calc-spar be laid upon it, the dot will appear double, and on moving the crystal round, one image will be seen to revolve round the other. By changing the position of the eye, the distance between the two images of the dots will be found to change; it will be greatest when the eye is in a line connecting a solid angle and the centre of the opposite plane; but to efface the double image and obtain single refraction, new surfaces would require to be cut perpendicular to the principal axis. In a natural crystal there are, therefore, always two images of an object seen through it.

In the remaining three classes of crystals, where the rhombic octohedron, whether right or oblique, gives the predominant character to the forms, the existence of a molecular constitution, regulated by the same cause as the external figure, is displayed in a peculiarly striking manner. There is no longer a single line in the crystal, in which ordinary refraction alone occurs, but there are two such lines, or axes of simple refraction. These axes, however, do not now coincide with the principal crystalline axis, as was the case when there was only one, but their position is so dependant on that of the crystalline axes as to show that they are the resultants of the forces which emanate from them, and which govern all the molecular actions of the crystal. If the ray of light does not pass exactly along one of these axes, but at some distance from it, it is divided into two rays; and of these rays, both follow new and peculiar laws of refraction, the proportionality of the sines being totally abandoned. The real distinction of the crystalline systems is thus completely proved by the existence of these remarkable optical properties by which they are characterized; and so perfect is this distinction, that in cases where the external form and cleavage would lead us totally astray, the optical properties of the body may show us its true crystalline position. Thus the mineral boracite (borate of magnesia) crystallizes in cubes, which are remarkable, however, for an anomalous replacement of the opposite solid angles by triangular planes. When, however, boracite was optically examined, it was found to possess double refraction, and to appear cubical only from the accidental circumstances of its rectangular axes being exactly equal to each other.

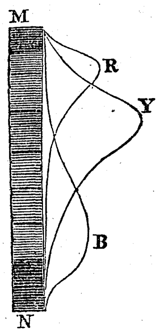
When a ray of white light, S, P, admitted into a darkened room through an aperture, H, passes into a refracting substance, *a*, A, B, C, whose surfaces are parallel, its path after refraction is parallel to its original course, and the ray continues white; but if the surfaces of the refracting medium be not parallel, if it be a prism, A, B, C, the ray of white light is separated into a number of rays of light, of different colours and of different refrangibilities, as at *g*; and if it has been derived from the sun, in place of a round white image, P, there is formed a series of solar images of different colours, which, overlapping each other, produce a long band, which is termed the prismatic *spectrum*, or image of the sun. The order of colours, the same as that seen in the rainbow, is, commencing with the rays of greatest refrangibility, violet, indigo, blue, green, yellow, orange, and red; the length of the spectrum, and the space occupied by each colour, varying with the nature of the refracting body, according to what is termed its *dispersive* power. White light is, therefore, not a simple, but a highly complex phenomenon, con-



sisting of impressions made simultaneously on the eye by the lights of these various colours. This may be verified by experiments of very simple performance: if a circular disk be painted with the colours of the spectrum, in segments proportional to the spaces which each colour occupies in the length of the spectrum, and then be made to revolve rapidly on a central axis, the eye loses the sensation of the individual colours, and a uniform grayish-white tinge is produced: if we had colours as perfect as those of pure solar light, their reunion would form pure white, and this actually may be produced by receiving the spectrum on a lens, by which all the coloured rays are brought to bear upon a single point, the focus, where reproduction of the original white light takes place.

Herschel has recently discovered that there exists in the spectrum, beyond the limits of the violet rays, other rays of a still higher refrangibility, and of a colour which he proposes to term lavender. This lavender light cannot be merely a weaker form of violet light; for, on concentrating it by means of a lens, it remains still unaltered, and appears to have no tendency to assume a violet tinge when it becomes more intense. If this proposal be adopted, there are then eight prismatic colours; and although some peculiarity of vision, with regard to colours, may cause a difference of opinion, yet the evidence obtained by Herschel of the real existence of simple lavender-coloured light appears to be satisfactory.

Of the seven prismatic colours, there are four which cannot be considered as simple lights, but as being formed by the mixing of rays of two different colours having the same refrangibility: these are orange, green, indigo, and violet; the first being the mixture of the superposing extremes of the red and yellow, the second of the yellow and blue, and the third and fourth of blue with red remaining in excess. There are, in fact, blue, red, and yellow lights spread over every portion of the spectrum; and if they were so in equal quantities, the spectrum would be white, and we could not have any decomposition of light by refraction; but, although there are blue rays of every degree of refrangibility, yet the larger proportion of them have a refrangibility greater than those of any other colour, and they are hence collected nearer the upper extremity of the spectrum. A portion of red light is spread also over the whole surface, but the majority of the red rays, having low refrangibility, are thrown to the opposite extremity, while the great proportion of the yellow rays, having a mean refrangibility, occupy the centre. In every portion of the spectrum there is therefore mixed, blue, red, yellow, and hence white light; but where these simple lights prevail, the colours of the spectrum are produced, and where two are present in excess over the quantities which form white light, the secondary colours, orange, green, indigo, and violet, are formed. The intensity of these spectra of simple light in each portion of the prismatic spectrum is represented in the figure by the distance of the curved lines, R, Y, B, from the ground, M, N. Where the red rises beyond the yellow and blue, the red space of the spectrum is produced; where the curve of the yellow light prevails, the space is coloured



yellow, and similarly in the blue; at the point where the curves of the red and yellow meet, the tint is orange; where the yellow and blue are equal, the colour produced is green; and where the red and blue are both in excess over the intermediate yellow, there is violet.

This view of the constitution of the solar spectrum, leading to the remarkable and unexpected consequence that there may be white light unalterable by the prism, its coloured rays having all the same degree of refrangibility, was obtained by Brewster, by means of the absorbing power of coloured bodies. If a ray of white light be incident upon a glass coloured red by suboxide of copper, it is decomposed in passing through it, the yellow and blue lights being intercepted or absorbed, and the red rays alone being transmitted. A glass does not possess this property of absorbing certain kinds of light, because it is coloured; but it appears coloured to our vision, because it acts so upon white light. The colours so given to glass are of great importance, from the use which is made of them for ornamental purposes in the arts; but they afford also to the chemist one of the most delicate and most certain means of detecting many metallic substances, thus:

Cobalt is known by colouring glass blue.				
Nickel	"	"	"	orange.
Chrome and vanadium			"	green.
Copper	"	"	"	green or red.
Iron	"	"	"	yellow or green.
Manganese		"	"	purple.
Silver	"	"	"	yellow or orange.
Gold	"	"	"	crimson.

And these are not the only cases in which colours are produced.

The colours of chemical compounds are so varied, that there cannot be laid down any principle by which they could be arranged: thus, lead forms with other simple bodies compounds which are brown, or red, or yellow, or white; mercury has a still greater range. There are, however, certain general facts worth bearing in mind, in which classes of bodies, to a certain extent, are characterized by colour: thus, the ordinary compounds of copper are usually green or blue; those of nickel, green; those of cobalt, pink or blue; those of chrome, green or purple. A singular property of certain bodies consists in what is termed *dichroism*, that is, when seen by light which has passed in different directions, they appear of different colours, which are often complementary, or such as, when mixed together, would form white light. This dichroism occurs only in crystals which refract doubly, and in which the absorption takes place unequally along the two refracted rays.

The colours of natural bodies, seen by transmitted light, depend thus upon the analysis which they effect of the light incident upon them, and of which they absorb one portion and transmit another Where the object is seen by reflected light, its colour is generally different from that given by transmitted light, for it frequently reflects, in considerable quantity, the light which it does not transmit Thus, solution of litmus, when seen by transmitted light, is of a rich reddish purple, but, seen by reflected light, of a fine, pure blue. In general, a portion of the light is reflected from the second sur-

face, tinged like the transmitted portion, which, mixing with that properly reflected at the first surface, modifies its colour. The transmitted and reflected lights are sometimes truly complementary; thus, sea-water, seen by reflection, is of a fine green, but the light which it transmits is pink.

When a ray of light is reflected from any surface at a particular angle, which is for glass 56° 45′, and for water 53° 11′, it acquires peculiar properties which it had not previously possessed, and is said to be polarized. If the ray be then made to fall upon a second reflecting surface, the effect varies according to the position of the plane of the second reflected ray. The reflection, if it be in the same plane as the first, is complete; but if it be at right angles to the first, there is no light reflected: in intermediate positions, the quantity of light reflected varies according to the angle which the second makes with the original plane. Light is thus said to be polarized by reflection. In all cases of reflection there is some of the light thus modified; for, although the angles above mentioned are those at which alone the polarization is complete, at all other angles the light reflected is partially polarized in a degree, according to its deviation on either side from the proper angles.

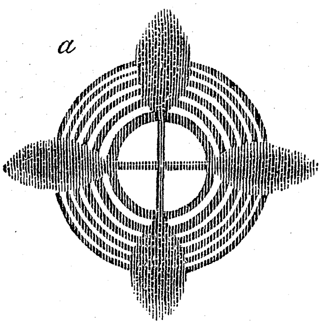
Polarization may be effected by various other means, as by refraction or absorption. Even in ordinary refraction some of the light transmitted is polarized, but it is mixed with so much ordinary light that its properties are obscured: however, if the same quantity of light be refracted often, it may be polarized completely; and hence, transmitting a ray of ordinary light, at a certain angle, through a pile of parallel glass plates, is a usual mode of polarizing it. In double refraction, the polarization of the refracted light is perfect, and the two emergent rays are found to be polarized in planes at right angles to each other. If these proceed together to the eye, they mix again, and thus recompose the original ray of common light; but by contrivances, such as in Nichol's prism, one may be turned aside or absorbed, and then the other used. In polarizing light by absorption, the mineral tourmaline is generally used; this is a doubly refracting substance, of such a nature that it absorbs completely one refracted ray and transmits the other. It therefore gives only a single image of any object, but this image is formed by light completely polarized. If two pieces of tourmaline be laid together, and the direction of their crystalline axes be the same in both, they act similarly upon the light, and, the same polarized ray being transmitted by both, the brightness of the image is almost the same with the two as with only one; but if they be placed with their crystalline axes at right angles to each other, the ray that is transmitted by the first is absorbed by the second, and no light can pass. If a ray of light be polarized by reflection or refraction, it is known that the polarization has been complete when the ray is totally absorbed by a tourmaline, the axis of which is perpendicular to the plane of polarization of the ray.

When a ray of light so polarized passes through a doubly refracting substance, it undergoes double refraction like a beam of ordinary light, being divided into two rays, polarized in two new planes at right angles to each other; and when these two rays are received upon another polarizing instrument, they are each divided into two portions, again at right angles, which unite, as the planes of polarization coincide two and two, and by their union produce some of the most beautiful phe-

nomena in optics; for as, in the doubly refracting substance through which the ray has passed, the two portions move with different velocities according to the refractive indices of the body, one issues in advance of the other by a certain distance, and according to this distance, which depends on the difference between the two refractive indices of the body, a series of colours is produced the most gorgeous that can be imagined, for every little difference of thickness a different colour is shown; with the same thickness the colour passes through all the prismatic tints, according as the plane of polarization of the ray of light is altered, and thus the action exercised upon the ray by the doubly refracting substance, shows itself in a manner equally beautiful and strange.

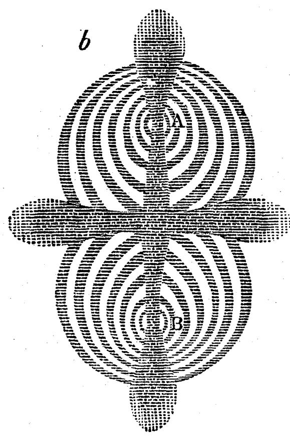
The apparatus used, in so employing polarized light to exhibit these properties of bodies, consists in, first, a means of polarizing the ray, which may be any of those before described, but which is generally a flat plate of obsidian or blackened glass, by which a polarized reflected ray is given. The substance to be examined is supported upon a frame, in a plane perpendicular to the direction of the ray; or, if it be fluid, a glass tube is filled with it, and, being closed by plates of glass with parallel surfaces, it is so placed that the ray shall pass along the axis of the tube. The ray, after emergence, is examined in order to detect the modifications which it has undergone, by an apparatus termed the analyzing piece, which may be, where two images are required, a doubly refracting prism, or, where only one, the Nichol's prism, a doubly refracting prism in which one image is destroyed; a tourmaline might also be used, but the brown or olive colour which tourmalines possess would deprive the phenomenon to be observed of much of the interest it derives from the beautiful display of colours.

a

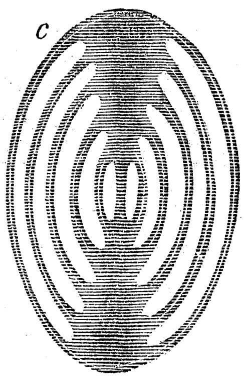


In nothing is the action of polarized light so interesting as in the evidence which it gives of the internal constitution of crystals of the different systems that have been described; for the real difference of molecular arrangement in crystals belonging to these various systems, is rendered still more remarkably distinct by the action which they exercise upon light in this peculiar state of plane polarization. If a ray of polarized light pass along the principal axis of a crystal belonging to the rhombohedral or to the square prismatic system, and on issuing be examined by means of an analyzing plate, the axis of the crystal is seen to be surrounded by a series of beautifully rainbow-coloured rings, the centre being occupied either by a cross which is alternately black and white, according as the analyzing plate revolves, as with calc spar, fig. *a*, or a circular space which is occupied successively by a series of colours similar to those which form the rings, as in quartz.

b



c



If the crystal belong to any of the more complex systems, and its optical axes be not much inclined to one another, there will be seen, on transmitting a ray of polarized light along the crystalline axis intermediate to the two, a double system of rings, which, uniting, form a very beautiful curved figure, such as is represented in figure *b*, which is the phenomenon as seen with nitre. The curves are crossed by two bands, black or white, according as the analyzing plate revolves, but which, when the crystal is turned round on its principal axis, open out, revolving each on its axis, A or B, and

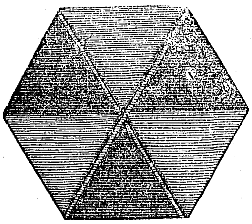
bend with the convexity towards the centre of the figure. In substances, as topaz and carbonate of soda, where the axes make a large angle with each other, the complete system of rings cannot be at once seen, and only one half, or the portion round one axis, as in the case of topaz in figure *c*, is visible in one direction. The angle of the axes in topaz is 18° 30′, but in other cases it may be much greater; thus with green sulphate of iron they are at right angles with each other.

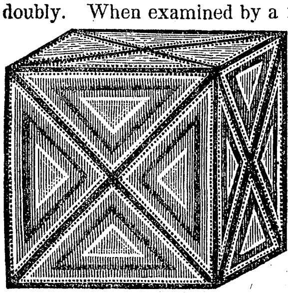
The physical production of these beautiful phenomena involves optical principles too recondite to be here introduced. It is, for the purposes of the chemist, sufficient to say that they arise from the mutual action of the two rays, which are produced by the double refraction of the crystal; and hence, if there be not double refraction, there can be no colours produced. With crystals of the regular system there is consequently no such result, and hence such crystals are recognised by the complete absence of coloured rings.

The optical properties of the different systems of crystallization may be thus summed up.

1. Regular system.	Single refraction.	No rings by polarized light
2. Rhombohedral system . . 3. Square prismatic system . .	Double refraction with one axis.	Simple system of rings by polarized light.
4. Right prismatic system . . 5. Oblique prismatic system . . 6. Doubly oblique prismatic system	Double refraction with two axes.	Double system of rings by polarized light.

When crystals form in a crowded or confused manner, it frequently happens that not merely are their surfaces modified in a complicated way, but that several crystals become soldered together so completely as to simulate a single form which does not belong to the substance of which the crystal is composed. These crystals are called *macles*, or twin or hemitrope crystals. Some bodies have a remarkable tendency to crystallize in this way; thus, sulphate of potash had been long considered as crystallizing in six-sided prisms, terminated by six-sided pyramids; and such crystals of it occur with almost exactly the proportions of the rhombohedral system; but by optical examination, this figure was found to be composed of three or six of the true crystals, which are right rhombic prisms of the fourth system. These being laid together, form, by their angles exactly joining, a six-sided prism; but when tested by polarized light, they show, in place of the system of rings which a true crystal should produce, the tesselated structure of the figure. In many cases, the agglutination of the crystals is less complete, and irregular figures, with the sides channelled by the imperfect joints, are found. A substance which illustrates remarkably this tendency to the macled form is the mineral analcime, which is termed also cubizite, from its forms belonging most perfectly, so far as external characters go, to the regular system. It has, however, no distinct cleavage planes, and refracts doubly. When examined by a ray of polarized light, the cube of analcime gives a most beautiful appearance. The diagonals of each surface become occupied by lines, which are alternately black and white, according as the analyzer is made to revolve, and in the intervening triangular spaces the richest colours of the rainbow succeed one another, according to the optical laws. This crystal is therefore made up of a great number of other crystals belonging to some one of the more complex systems; but its structure is so extraordinary, that the determination of the form of its real crystal has been as yet impossible. In this instance, and in that of boracite already noticed, the optical properties have been the means of showing the true nature of bodies which, from their external form, should otherwise have been ranked among those which crystallize in the forms of the regular system.





It has been noticed as a general character of the crystals of the rhombohedral and square prismatic systems, that by the analysis of a beam of polarized light transmitted along the principal axis, there is seen a system of coloured rings traversed by a cross, alternately black and white, as the analyzing plate revolves, but

farther, that in the case of quartz the cross is not produced, the central space being occupied in succession by all the prismatic colours. Even in quartz there have been found two modifications of this property; with one, the analyzing plate must be turned from right to left, to obtain the spectral colours from red to violet; but with the other, the rotation must be in the opposite direction, to show them in the same order. The molecules of the quartz cause these colours to appear along the axis by turning the plane of polarization of each colour round in a different degree, and thus opening out into a fan shape those combined lights, which had previously affected the eye only as white or black. This faculty does not depend upon the manner of arrangement of the particles of the quartz; it involves the chemical nature of the molecules; and, although some observations appeared to connect it with the crystalline structure, it is now fully established to be independent of it. In fact, this property of *circular polarization*, as it is termed, belongs to certain bodies, independent of their arrangement, and even in many cases accompanies them when they enter into combination. It is even found in liquids, particularly the volatile oils; and when oil of turpentine is converted into vapour, its molecules preserve unaffected their rotative power. Its existence is, however, subjected to remarkable anomalies; thus, when oil of turpentine combines with muriatic acid and forms artificial camphor, it retains its power of rotation; but when the artificial camphor is decomposed and the oil of turpentine got back again, its power of changing the plane of polarization of the ray of light has totally disappeared.

[These phenomena of circular polarization may be readily traced. If from a crystal of quartz a disk is cut transversely, a system of rings will be seen enclosing a circular coloured space. If the disk be turned round, no change takes place; but if the analyzing plate turns, the colour passes through a series of tints, which, after 100° of rotation, may end in a sombre violet. If, now, we cut from the same crystal another disk twice the thickness of the former, and make use of it, we shall find the tint different from what it last was; but, by turning the analyzing plate 100°, we may bring it back again to the same sombre violet: with a plate three times as thick, we should have to turn 100° still farther to produce the same tint, and for each additional thickness an additional 100°. We therefore infer that, when polarized light passes along the axis of a crystal of quartz, its planes of polarization rotate circularly, or, rather, spirally, in the crystal; and this takes place in some specimens from right to left, and in others from left to right. Under these circumstances, light is said to undergo circular polarization.]

In cases, therefore, where bodies exhibit this action upon light, their power of rotation becomes an important numerical fact in their descriptions, and it may be measured by the angle through which a certain thickness of the body is capable of moving the plane of polarization of a ray of homogeneous light, such as the pure red given by glass coloured by sub-oxide of copper. It may also be expressed, when white light is used, by the angle at which the pure violet is produced, and the direction of rotation is expressed by an arrow turned either to the right or left, according as it is necessary to make the analyzing crystal revolve to the one or the other side. Thus, the rotative power of oil of turpentine, contained in a tube six inches long, is for red light 45° $\longleftarrow$, and of oil of lemons, in the same length, 84° $\longrightarrow$. The rotative power of quartz is about 68·5 times greater than that of oil of turpentine. This property is beautifully applied to trace the changes which occur during the saccharine fermentation: a solution of starch possesses a high $\longrightarrow$ power; but it gradually changes into the sugar of grapes, the rotative power of which is $\longleftarrow$. Hence the action of the starch, when fermentation has commenced, rapidly diminishes, until there is so much sugar formed that the $\longrightarrow$ and $\longleftarrow$ exactly balance, and the solution is totally without action upon a polarized ray; after that, the quantity of sugar still increasing, the rotation becomes $\longleftarrow$, and increases until all the starch has been decomposed. With such a solution, knowing the total quantity of starch originally dissolved, the measure of its rotative power enables the quantity of sugar present to be at once calculated. The juices of plants which contain sugar, as the beet-root, the maple, the sugar-cane, may be exactly valued by a simple determination of their rotative power compared with their specific gravities. This property of the circular polarization of a ray of light, which at the first aspect might appear so far removed from proper chemical inquiry or useful application, becomes thus an instrument from which the distiller or sugar-boiler may every day derive advantage; and when we come to discuss the means by which we endeavour to learn the internal constitution of bodies produced by chemical affinity, we shall find that the light which ordinary polarization throws upon

the internal mechanical structure of the crystal is not more brilliant than that which we obtain of the arrangement of the chemical constituents by their circularly polarizing power.

Some specimens of quartz appear destitute of this rotative power: the purple quartz, amethyst, is generally so, and gives with polarized light the ordinary black cross. But these peculiarities of quartz are related to their crystalline arrangement. Thus, in those specimens which possess rotative power, the solid angles of the pyramid (*k*, page 28) are generally replaced by planes which are unequally inclined to the axes; and where these planes are present, the direction of the rotation can be foretold, it being to the right or to the left, according as these unsymmetrical faces are inclined. Such crystals are termed *plagihedral;* as in the cases where no such faces can be traced, the rotative power is generally absent, and this arises, as is remarkably evident in amethyst, from the crystal being formed of separate crystals rolled up together; and as these may possess opposite rotations, and so neutralize each other, the action on light should be like that of calcareous spar, which has no rotative power. Such crystals are truly macles; and hence the circular polarization may show a still more intimate crystalline arrangement than could be detected by light in its ordinary polarized condition.

With such an example, it was not difficult to conclude that the power of rotation depended on the crystalline arrangement, particularly as quartz, in all its uncrystallized conditions, is devoid of all rotative power; and, accordingly, until the discovery of the power of rotation in liquids, and that this property was found to accompany the molecules of the body through all states of aggregation, it was considered to have its origin in the mechanical structure of the body; but we must now invert the argument, and infer that the difference of rotative power in right-handed and left-handed quartz does not result from the difference of crystalline arrangement, but that this last is caused by actual difference of properties in the molecules themselves, of which the most remarkable is detected by the opposite actions upon light.

The impression of light was at one time considered to be produced by a series of exceedingly minute particles, of a peculiar substance, emanating from the sun and from burning or luminous bodies, and which strike upon the eye. This idea has been, however, now almost totally abandoned, and all the phenomena are considered to arise from the vibrations of an exceedingly attenuated medium, thrown into waves by luminous bodies of every kind, and which, filling all space, and being diffused through the substance of the most solid bodies, and occupying the spaces between their more substantial molecules, transmits and modifies these vibrations, and confers upon substances transparency or opacity, colour, and all other properties of acting upon light which they may possess.

This medium, or luminiferous ether, as it is termed, is supposed capable of vibrating in waves of different lengths, and from this difference in length of wave arises the difference in colour of the light produced. The shortest wave produces violet, the most refrangible light; the longest wave, red, the least refrangible light: the length of the wave being in all cases inversely proportional to the refrangibility of the light. The impression of the different colours arises, therefore, precisely as the impression of different sounds is produced, by a difference in the length of the waves in the vibrating air; the shortest wave, in sound, giving the highest note and in light giving the violet colour The actual length of these waves of light is extremely small: for violet light there are 57·490 in an inch; for red, 39·180; the average of the different colours being 50·000; and hence, in white light, there acts upon the eye in every second 610·000000·000000 luminiferous vibrations.

In the case of doubly refracting crystals with one axis, that is, those belonging to the rhombohedral and the square prismatic sys-

tem, the elasticity of the ether is supposed to be so far modified by the arrangement of the molecules of the body, that the velocity of propagation of the waves is more rapid in one direction than in another at right angles to it, and hence there are two refracted rays. In the three systems, the crystals of which have double refraction with two axes, the elasticity of the ether is supposed to be different in each of three perpendicular directions, and hence neither refracted ray can follow the ordinary law. It is thus, as has been already stated, that the classification of all crystallized bodies in these systems is shown, not to be an arbitrary assumption, but a principle based upon our most decisive evidence of molecular arrangement.

The rays of light derive some of their most remarkable properties from the principle that the vibrations are accomplished in a direction perpendicular to the direction of the rays. Thus, if we conceive a ray of light moving from north to south, the little vibrations which constitute it are effected in a direction east or west, and in every other direction equally perpendicular to its path; and ordinary light is characterized by the fact that its vibrations are accomplished in every imaginable plane. If we reduce these vibratory movements to a single plane, the light becomes polarized, and is then in the condition for dissecting the interior of crystallized bodies, and exhibiting the beautiful illustrations of their structure that have been already noticed. But it would lead us too far away from our proper subject to enter into the description of polarizing apparatus, or even of its principles, in detail, as the indication just given of its nature is sufficient.

Perhaps the most remarkable and the most important principle of the theory of waves is, that two portions of light may act on each other so as to interfere and produce darkness, though at another point they may form light of double brilliancy. To effect this, it is only necessary they should be in opposite states of vibration, that is, while the waves of one ray should be rising up, those of the other should be falling down: these motions then compensate each other, and the result is the same as if no vibratory motion had existed, that is, as if no light had arrived at the points where the rays met. It is only, however, when one of the simple coloured lights is employed, that actual blackness occurs by the mutual destruction of the rays: if white light be used, there is produced a brilliant series of prismatic colours; for at the moment when the red light is destroyed, the remaining blue and yellow form a bright green; when the yellow is destroyed, the red and blue produce a purple. Cases of this kind of interference are extremely common: it is thus that the coloured rings of crystals, and the colours of the soap-bubble or oil-film are produced. The brilliancy of the plumage of birds, the lustre of many minerals, as of labradorite, arise from the interference of the portions of light which after reflection thus act on each other.

Under ordinary circumstances, light is always associated with heat; the sun, the source of warmth to the surface of our globe, being also the natural origin of light: and in most cases where light is artificially produced, it is associated with heat, which is also ca-

pable of being transmitted in a radiant form. It was, indeed, once considered, that at certain temperatures heat became converted into light, and that the colour of the light depended on the degree of heat; a body, when first rendered luminous by being heated, emitting a dull red light, which gradually becomes brighter as the temperature rises, until at the highest degree of heat the light emitted is pure white, and similar in constitution to the solar ray. The powers of emitting heat and of emitting light are, however, although so frequently associated, quite independent and distinct; and the rays of heat and those of light may be perfectly separated from each other. It would anticipate too much the account of radiant heat to describe the means of separating the heating from the luminous qualities of ordinary light; but elsewhere they will be described in full. A body may become luminous when very moderately heated, as is the case with many minerals, as fluor spar Light may be produced also by the friction of bodies, as by rubbing two pieces of sugar briskly together, or by striking together two pieces of quartz; and in these cases it is difficult to assign its true origin, as, possibly, a minute trace of the substance may be very intensely heated. There are also many bodies which, when exposed to the light of the sun after having been made red hot, appear to absorb a portion of it, and become capable of emitting it slowly, giving a pale bluish light for some time afterward in the dark. This occurs particularly with chloride of barium, native sulphate of barytes, carbonate of lime, and a great number of other bodies. Such substances are said to be *phosphorescent*. Thus fluor spar is rendered so by heat, sugar and quartz become so by friction, and the electric spark is capable of conferring the phosphorescent property on a great variety of bodies.

Organized substances become phosphorescent in the first stages of their decay; thus, rotten wood, and fish before actual putrefaction has commenced. The light emitted is, in such cases, the result of an exceedingly slow but distinct process of combustion; it requires the presence of atmospheric air, or oxygen, although an exceedingly small quantity may suffice, and it is extinguished and revived by all such means as facilitate or retard the chemical action of the air upon organic bodies. The light emitted by the glowworm and the fireflies, as well as by the great variety of marine zoophytes, appears also to be not merely an evolution of light as a product of vital action, but to arise similarly from the secretion of a substance, which, slowly combining with the oxygen of the at mosphere, produces the light as a consequence of combustion Animal phosphorescence is, therefore, to be ascribed to chemical action.

The white light, derived from different sources, does not always possess the same physical constitution. If the coloured spectrum produced by the solar ray be closely examined, it will be found crossed by a multitude of black lines, indicating the total absence in the sun's light of rays of certain refrangibilities. That this is inherent in the light is shown by the fact, that when we change the nature of the prism, the position of the space in which these black lines occur may alter, but the lines preserve all their relative

distances from each other totally unchanged. Hence, in place of referring to the colours of the spectrum in order to characterize its properties, those lines, of which the most remarkable is a double line situated in the yellow space, are used as marks. The light of the sun, of the moon and planets, as well as white light produced by our processes of combustion, all consist of the same elements of yellow, red, and blue, and all are distinguished by the same set of lines. In the light of some of the fixed stars the same lines are found, as is the case with Pollux; but in the spectrum formed by rays from Sirius or from Castor, this double line does not occur, but is replaced by one broad line in the yellow space, and two remarkable dark lines in the blue. It is very curious, that if we examine the spectrum through certain coloured media, as the vapours of iodine or bromine, we find additional black lines, and by using gaseous nitrous acid these become almost innumerable, and increase so much when the gas is heated that the spectrum is obliterated and the gas becomes opaque. It is possible that such takes place at the origin of the light of the heavenly bodies, and that the sun and the fixed stars are involved in absorbing atmospheres, which allow only certain rays to pass, and that hence there may exist in nature kinds of light from which the eye of man is screened forever by means of such an impervious veil.

Some classes of chemical substances are, to a certain extent, characterized by the facility with which they are decomposed when under the influence of light. The salts of silver, of gold, of platina, and, in some instances, of mercury, are subject to this influence. A great variety of vegetable and animal bodies undergo important changes in their constitution by the action of the solar rays, the development of certain colours requiring the agency of light, and the majority of colours being destroyed when its action is too great: hence the fading of dyes arises. The power of light thus to modify the affinity by which chemical combination is produced, has been found to be exercised specially by the violet or more refrangible extremity of the spectrum, and even with great intensity by invisible rays quite outside of the luminous space, and extending beyond the lavender-coloured prismatic space of Herschel. It has been also considered that the rays of the red extremity of the spectrum possessed chemical properties of an inverse kind, and that the decomposition produced by violet light might be counteracted, and the elements brought to recombine by the red rays. This is not certain. All that has been established is, that there exist in solar light, and probably in all light derived from sources of combustion, three distinct sets of rays, the one of proper light, which produces only luminous effects, the second of radiant heat, the nature of which will be specially examined in the following chapter, and the third of rays which, though neither luminous nor heating, exercise an influence on chemical affinity, and the nature of which will be discussed with more detail when the subject of chemical affinity and its relations to the other physical forces has been described.

CHAPTER III.

OF HEAT CONSIDERED AS CHARACTERIZING CHEMICAL SUBSTANCES.

At almost every step of chemical inquiry it is necessary to introduce the action of heat, either as modifying the results of the chemical action of bodies upon each other, or as affording characters by which the substances we operate upon may be distinguished. The doctrine of heat and the history of its effects have consequently, at all periods, formed an important portion of the studies of the chemist; and it is, indeed, only lately, since the brilliant course of discoveries that was opened, and so successfully prosecuted by Melloni and by Forbes, has identified the theories of heat and light, that this subject has been contemplated in its proper aspect as a physical science, and its application and influence in chemistry have ceased to be considered as making up the science, properly so called, of heat.

Of all the physical sciences, however, that of *Heat*, or *Thermotics*, as it is now termed, is the most important to the chemist in guiding him in his operations, and in the accurate description of their results. On this account it will be necessary to describe the properties of heat more in detail than those of any other of the physical agents, and to illustrate these properties by more numerous references to cases in which their utility in chemistry is apparent.

The effects of heat, by which, according to their degrees, bodies may be characterized, are,

1st. Change of volume for a given change of temperature. *Expansion.*

2d. Quantity of heat required to produce a given change of temperature. *Specific heat.*

3d. Temperature necessary for liquefaction. *Melting points.*

4th. Temperature necessary for giving a certain elasticity to a vapour. *Boiling points.*

5th. Quantity of heat required to produce a given change of aggregation. *Latent heat of liquids and vapours.*

6th. Manner and rapidity of communicating or receiving heat. *Conduction and radiation of heat.*

The subject of heat will therefore be studied specially under these heads; and it will be necessary to introduce an account of our mode of measuring heat and temperature by the thermometer and pyrometer, and to add some observations on the physical relations of heat and light, and on the physical theory of heat.

SECTION I.

OF EXPANSION.

When describing the effects of cohesion, I have already noticed that the molecular constitution of all bodies might be considered

to depend on the relative power of the attractive force, *cohesion*, and the repulsive force of *heat*, upon their particles. That where the attraction was in excess, the molecules were knitted firmly together to form a solid body; but that where repulsion was most powerful, all cohesion was lost, and the body assumed the form of a vapour or a gas. In the intermediate condition, where the forces appeared to be nearly in equilibrium, the liquid state was produced, in which the molecules of the body appeared still to unite by a trace of remaining cohesion, but that they moved among one another with perfect ease, and the slightest external force might disarrange them entirely. Now the change from one to the other of any two of these conditions is not quite abrupt. If a cold body be gradually heated until it shall begin to liquefy, its particles do not remain in the same condition up to the moment when they separate so far as to change their state of aggregation; on the contrary, from the instant that the substance becomes warm, the change begins; the molecules of the body gradually separate, occupy more space than before, and from the very commencement of the increase of heat, the body, though it may remain solid, *yet expands*. In the same manner, if a liquid be heated, the change of aggregation does not commence until the increase of heat has reached a certain degree; but from the beginning a change of volume occurs, the increase of which marks the gradual diminution of cohesion. In gases there can take place no farther change of form, and the only effect which heat can produce upon them is expansion.

This power of repulsion which we suppose heat to exercise, in causing the transition from one state of aggregation to another, as well as the expansion which occurs without change of form, may become directly evident to the senses, at least in a partial way, in many cases. Thus, many powders, if sprinkled on a warm capsule, or, still better, on a silver plate, are thrown into violent motion, and dissipated by the mutual repulsion of their particles, independent of any currents of air which might affect them. When liquids, particularly alcohol and the oils, are brought to boil, the drops which are mechanically thrown up out of the liquid do not mix with it on falling back, but roil about on the surface, and appear to repel each other, and to be repelled by the hot glass of the vessel in a remarkable degree. If a brass poker, strongly heated, be allowed to rest against a cold iron bar, or, still better, if a rounded bar of brass be made very hot and laid upon a flat block of lead, the surface of the cold metal becoming heated, repels the warmer brass, which instantly falls down again, by its weight overcoming the repulsion, when the metal cools. When the brass again touches the metal or lead, the latter is again heated at the point of contact, and again there is repulsion succeeded by a new contact, and these repeated motions throw the bar of brass into a state of tremulous agitation, which being conveyed to the ear by the intervening air, gives a remarkably distinct and agreeable musical tone. The better conductor, the heated body, and the worse conductor (provided both are metals), the cold body can be, the more successful is the result.

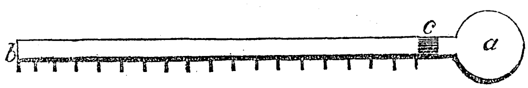
This force of repulsion is made still more distinct, and even measurable, by an experiment devised by Powell. When a flat and a convex glass plate are strongly pressed together, they still do not touch, but are separated by an exceedingly thin space, by the action of light on which there are produced coloured rings, like those seen on the surface of a soap-bubble, or in a film of oil floating upon water. Each colour belongs to a distinct and measurable thickness of this space; and when such an apparatus is gradually heated, the rings close in towards the centre, showing that the glass plates recede from one another, and the degree of repulsion may be determined from the narrowing which occurs in the breadth of any particular coloured ring, according as the temperature rises.

In gases, the expanding effect of heat is unaffected by any disturbing cause; there is no cohesion remaining to impede its oper-

ation; hence a certain increase of heat affects all gases alike; and no matter how hot or how cold a gas may be, a certain increase of heat produces the same increase of volume in every case. In solids and in liquids, however, it is different; the expansion which occurs is but the result of the opposing forces of cohesion and of heat, and hence the amount of expansion depends not only on the quantity of heat which is applied, but also on the power of cohesion by which it is resisted, and which depends upon the nature of the body. Consequently, every fluid and every solid expands in a degree which is peculiar to it. There is yet another consequence of the influence of cohesion upon the expansion of solids and of liquids. Let us represent the cohesive force of a certain substance, for example, copper, by 10, and let us suppose that we apply to it a quantity of heat which will expand it through a space which we will call 1, and will diminish its cohesion from 10 to 9. If, then, we apply another quantity of heat exactly equal to the former, it will not have to contend against a cohesion of 10, but of 9, and will, consequently, be able to produce an expansion of more than 1, say $1\frac{1}{2}$, and it will reduce the cohesion more than it did before, as from 9 to $7\frac{1}{2}$. If, then, another equal quantity of heat be added, it having still less opposing force to overcome, will act still more powerfully, reducing, for example, the cohesion from $7\frac{1}{2}$ to 5, and the increase of volume becoming, in place of $1\frac{1}{2}$, 2. In solids and liquids, the rate of expansion increases thus, with the temperature, from the diminution of cohesion; but in gases, where the cohesion remains the same, or, rather, is completely absent, the expansion is proportional to the additional quantity of heat, no matter how much may have been sensibly present in the gas before.

I shall now proceed to consider in detail the rates of expansion of various bodies, commencing with those of gases, for which the simplest results have been obtained. Before doing so, however, it is necessary to study the means by which we ascertain the quantities of heat which we add or subtract from bodies to effect their expansion or contraction; to investigate, in fact, the principle on which the thermometer and pyrometer are founded, and such details of their construction as shall hereafter be found necessary to be known.

Let $a\,b$ be a glass bulb with a long and narrow neck, which is divided



by a scale, as in the figure, of which each division is a certain part, as $\frac{1}{1000}$ of the volume of the bulb. Let us suppose the bulb a to be filled with pure dry air, at the same degree of heat as that at which ice melts, and separated completely from the external air by means of a globule of mercury, c, which is exactly settled at the commencement of the scale. If, now, the instrument be warmed, the air in the bulb expands, and, according as it increases in volume, pushes before it into the tube the globule of mercury. This last serves, therefore, as an index of the increase of volume which the air gains as it is heated, and by its position we can read off the exact propor-

tion. If the source of heat be water boiling, under ordinary circumstances, at Dublin, at the level of the sea, as soon as the air has been heated to exactly the same degree as the water, the globule will be found to have arrived at the 365th division on the scale. Therefore, 1000 measures of air, on being heated from the degree of melting ice to that of boiling water, become 1365. Now as, from the constitution of air and gases, the effect of each increase of heat is the same, we may consider the whole quantity of heat which it received from the boiling water to be divided into 365 parts or degrees, and each of these parts being applied separately to the bulb, should have increased the volume of air by $\frac{1}{1000}$ part, or should have converted the 1000 volumes into 1001. There is thus obtained a scale of expansion which is quite artificial and arbitrary certainly, but which, having been once contrived, may be with perfect accuracy applied to measure different quantities of heat. Thus, if we warm water to blood heat, and immerse in it the air bulb as described, the expansion of the air will move the globule of mercury to the degree 122, which is almost exactly the one third part of the 365, and hence the water, in being heated from the degree of melting ice to that of blood heat, received almost exactly one third of the quantity of heat which should have made it boil, and its temperature is one third as high.

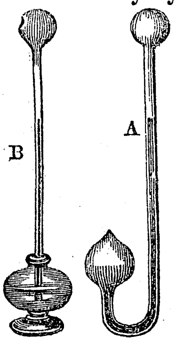
I have here spoken of measuring the successive quantities of heat which the air received, and in this case the manner of expression is sufficiently accurate, as well as the most simple. But it is necessary to explain the true meaning of the words quantity of heat and temperature. The amount of expansion which a hot body is capable of producing in the air or mercury of the thermometer, measures truly what is called its *temperature.* The temperature has nothing whatsoever to do with the quantity of heat which the body may contain, it refers only to its expanding power. If a quantity of water, of oil, of ether, of mercury, or of iron produce all the same amount of expansion in the air or mercury of the thermometer, we say they have the same temperature, without pretending to know anything of the quantity of heat which they may actually possess. The thermometer and pyrometer are therefore instruments for measuring, not heat, but *temperature*, and we denote by *degrees of temperature* the amount of expansion produced, marked off on any arbitrary scale which we may think proper to adopt.

Gases expanding more than any other bodies, the air thermometer is the most sensible that can be made, and in the form just described it is an exact measure of heat, subject only to one correction, which is, that although the air, in being heated from the degree of melting ice to that of boiling water, actually expands $\frac{365}{1000}$ of its volume, yet that expansion is not all visible, for the glass bulb expands also on being heated, although in a very small proportion, and holds $\frac{2}{1000}$ more than it did when cold; the visible expansion on the scale is therefore only 363 degrees, and this must be allowed for to have complete accuracy. The form of the air thermometer which has been just described is, however, quite unfit for ordinary use; the adjustment of the index globule, the necessity that the instrument should be perfectly horizontal, which is quite

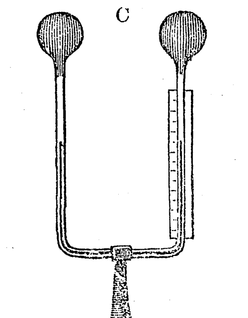
impossible in the majority of practical cases, renders this kind of an air thermometer too unmanageable; and since the air changes its volume very much for every change of pressure, and our atmosphere varies in its weight almost every hour, an air thermometer left open, as at the orifice *b*, would change continually without reference to the degrees of heat at all, and would thus give false indications. The end of the tube must therefore be accurately closed.

When, however, the air inside is thus confined, the simple rule of the dilatation being proportional to the increase of heat, ceases completely. For if the point *b* be closed, and the bulb *a* be heated, the globule of mercury, in moving along the scale, condenses the air before it, and thus generates an elastic force, by which the expansion is resisted and diminished in amount; the degrees would therefore be no longer equal, but rapidly diminish in size, so that on the upper parts of the scale they could not be distinguished from one another, and would hence be useless. But by having a second bulb, in the next figures, the elasticity of the air compressed in the cold bulb increases much less rapidly, and the scale to be applied to the stem connecting the bulbs is easily constructed. As the stems of these air thermometers are generally upright, mercury would be too heavy a fluid to introduce in a column, and the mere globule which we supposed in the example first taken would not answer, from the facility with which it might be broken or displaced: to any watery or spirituous fluid there is also an objection, that the amount of expansion would be increased to an uncertain degree by the portion of fluid converted into vapour. To avoid these errors, oil of vitriol may best be employed, and it is generally coloured red to render the motion of the fluid column more easily visible.

An air thermometer, closed perfectly, indicates a change of temperature only by the difference between the elasticity of the air in



the two bulbs. No matter how high or how low the temperature may be, if it affects both bulbs to the same degree, the air in each bulb presses on the liquid column with the same force, and exactly balances the other. The instrument indicates, therefore, such temperatures only as affect one bulb and not the other; the difference, in fact, between the temperatures of the two bulbs, and hence is properly called the *differential thermometer*. In fig. A the one bulb is much above the other In fig. B the stem which terminates above in a bulb is open below, and plunges into the fluid which the inferior bulb contains. This lower bulb is soldered or cemented at its orifice round the tube, so as perfectly to prevent the action of the air. Fig C represents



the most ordinary form; the bulbs are on a level, and are connected by a U-shaped stem.

The air thermometer is thus, in all its forms, liable to so many inconveniences from the limited range of its scale, if it be not open to the air, and from the complex form which the scale assumes if the external air be prevented from communication, that it is never made use of in practice except in some particular cases, which shall hereafter be specially noticed. We are therefore obliged to have recourse, for our accurate measures of temperature, to other bodies, which, though not so sensible as air, offer more practical advantages.

The liquids which are generally used to measure, by their expansion, change of temperature, are alcohol and mercury. The former, in being raised from the melting point of ice to that at which itself boils, expands $\frac{9}{100}$, whereas air within the same limits would have expanded $\frac{32}{100}$, being about three and a half times as much as alcohol: and mercury, in having its temperature raised from the melting point of ice to the boiling point of water, expands $\frac{18}{1000}$, or about $\frac{1}{20}$ of the quantity of air. Hence these liquids are much less sensible, as thermometers, than air; but their other advantages are decidedly in their favour. Alcohol is only employed where the object is to measure very great degrees of cold; and for this purpose it is admirably fitted, as it is the only liquid that has not yet been frozen. Mercury, on the other hand, may be applied to an extensive range of temperatures, as it freezes only by the application of an intense cold; and it does not boil until it arrives nearly at a red heat. It has the largest interval between its freezing and boiling points of any liquid that is known. Mercury is also admirably suited to be a measure of heat, by the accidental circumstance that its expansion, when contained in a glass bulb, is accurately proportional to the temperature, and its indications therefore absolutely true.

This is occasioned by the circumstance that, as in all liquids and solids the expansion increases with the temperature, the rate of increase of the capacity of the glass bulb exactly corresponds to the increase of the rate of expansion of the mercury, and absorbs it; so that the visible expansion of the mercury is uniform, and a degree in every part of the scale is of the same length. For instance, if mercury and air be together heated from the freezing to the boiling point of water, 1·000 measures of air become 1·365, and 10·000 measures of mercury become 10·180. If, then, they be both heated as much more, the air, expanding at the same rate, becomes 1·730; but the mercury, expanding more rapidly, becomes 10·363: and hence, if a scale was so applied, there would be shown 180 degrees in the lower, and 183 degrees in the upper part of the scale, to the same quantity of heat. This is corrected by the expansion of the glass bulb which holds the mercury. At the temperature of melting ice, the bulb holds, for example, 10·000 measures of mercury; but, on being heated to that of boiling water, it holds 10·026. The mercury, however, having become 10·180, the difference, (10·180—10·026)=154 measures, passes into the stem, and makes the rise of temperature upon the scale. When, now, the second portion of heat is applied, the mercury becomes 10·363; and the glass bulb, expanding at the same time, becomes able to hold 10·055: and hence the difference, (10·363—10·055)=308 measures, passes into the stem and moves along the scale. Thus the visible portion of the expansion is rendered exactly proportional to the increase of heat; and the mercurial thermometer becomes, not merely the most convenient, but the most accurate measure of heat which we possess.

In constructing a thermometer, the first requisite is, that the bore of the tube shall be perfectly uniform, for otherwise the result above described, which gives all

its real value to the quicksilver thermometer, would be completely inapplicable in practice. This is ascertained by finding that a small quantity of mercury, moved up and down the tube, occupies exactly the same length in every part. A proper tube having been thus obtained, one extremity is closed, and a bulb is blown upon it; another is formed near the open end, leaving a space between the two bulbs somewhat longer than the thermometer is intended to be. The tube and bulbs having been heated, are allowed to cool, with the open end immersed in pure and recently-boiled mercury. By the contraction of the internal, and the pressure of the external air, a quantity of mercury is forced into the first bulb, and ultimately the bulb at the closed end is filled completely by a repetition of the process. When the introduction of the mercury has been completed, the open end of the tube is closed by a little sealing-wax, to prevent the admission of air or dust, and the tube is allowed to cool with the terminal bulb down. When it has cooled completely, it is again heated to the highest degree it is intended to indicate; and the fine flame of a blowpipe being directed upon the point which is to be the extremity of the tube, it is melted, and the orifice completely closed. When the instrument then cools, there remains over the mercury in the stem a perfectly empty space.

It remains, then, to attach the scale. When describing the general principle of the thermometer, in the example of dry air, pushing, by its expansion, an index globule of mercury along the stem, the scale which included the interval from the freezing to the boiling points of water was supposed to be divided into 365 parts. This was, however, merely because the 1000 measures of air, in being heated through that interval, expand in that proportion. The scales that are actually used are different, although quite as arbitrary. The simplest scale is that in which the interval between the freezing and boiling points of water, which is universally taken as the standard, is divided into 100 parts; it is termed the centigrade scale, and is employed in France, and generally in Germany and the north of Europe. In it ice is said to melt at 0°, and water to boil at 100°. On the scale generally used in this country and Great Britain, the standard interval is divided into 180 degrees, but the melting point of ice is not taken as 0°, but as 32°, from a very absurd idea of Fahrenheit, who was the inventor of this scale. He mixed together snow and salt, and having thus produced a more intense cold than anybody before him had done, he imagined that he had attained a point at which the bodies had no heat at all, that he had arrived at what was afterward called the absolute zero, and he called that point 0°; the melting point of ice was then 32°, and water boiling at 180° higher, its temperature was marked 212°. There is another scale, sometimes, but not often used; that of Reaumur, in which the melting point of ice is the commencement or 0°, and the boiling point of water is marked 80°. The first step in the graduation is to mark the extreme points of the standard interval: the melting point of ice, and the boiling point of water. To do this correctly, some precautions must be taken. I have frequently spoken of the melting point of ice and the freezing point of water as meaning the same temperature, and under ordinary circumstances they do so; but they do not so necessarily. The freezing of water is a crystallization, and, like all other cases of crystallization, may take place with greater or less facility. If water be agitated, or if it be contained in rough vessels, affording prominences to which the crystals of ice may attach themselves, it freezes exactly at 32° on Fahrenheit's scale; but if the water be kept carefully at rest, and be contained in smooth glass vessels, free from dust, it may be easily cooled to 25°, and has been cooled even to 15°, without becoming solid. Hence, if we wished to determine the zero by means of freezing water, an error might easily be committed. Ice, however, under all circumstances, melts at 32°; and hence, by plunging the bulb of the thermometer into a mixture of ice and water, and marking on the stem the point at which the level of the mercury settles, the first fixed point upon the scale is had. To determine the second point, that at which water boils, it is necessary to attend to the condition of the barometer. It will be hereafter described how the boiling point of every liquid varies with the atmospheric pressure; it is here enough to notice, that either the boiling point must be determined when the barometer stands at 29·8 inches, or a correction, which will be hereafter given, applied for any difference of height which may exist. The water must boil also in a metallic vessel, for water in a glass or porcelain vessel has its boiling point somewhat raised, and as the thermometer is to be used for chemical purposes, the bulb and only a small portion of the stem should be immersed in the boiling water. The two fixed points having been thus obtained, the interval is to be divided into 180 equal parts or degrees for the ordinary scale of Fahrenheit, and then 32 of these degrees counted downward from the point of melting ice to obtain the zero; for the zero

cannot be truly got in the manner in which Fahrenheit is supposed originally to have invented it, for a mixture of snow and salt is found to produce always a cold of about 2° below zero, or —2°. As our range of temperature passes far below the zero of the scale, we count downward precisely as we count upward, only prefixing in the former case the — minus sign, whereas, in the degrees above zero, the + plus sign is usually omitted. Thus, +50°, or simply 50°, is fifty degrees above zero, but —50° is the same number below zero. To construct the centi grade scale, the method is precisely the same, except that we make the point of melting ice 0°, and that of boiling water 100°, and a degree being the $\frac{1}{100}$ of the interval, we count up and down from zero, precisely as in the other case.

It is generally proper to lay a thermometer aside for a few weeks after having filled it before proceeding to apply the scale. For it is found that as there is a vacuum in the instrument above the mercury, the external pressure acting on the thin glass of the bulb gradually changes its form a little, and would move up the fixed points, sometimes through one or two degrees, if they had been marked before the change.

The centigrade scale is of such extensive use in the works of most distinguished chemists, that it is well to show more closely its relation to the ordinary scale of Fahrenheit, and the means of reducing one to the other. The standard interval is divided into 180° Fahrenheit, and into 100 centigrade degrees, and hence a degree of the former is equal to $\frac{100}{180}$, or $\frac{5}{9}$ths of a centigrade degree. To reduce any interval in centigrade degrees to Fahrenheit's, it is therefore to be multiplied by 9 and divided by 5; and for the reduction from Fahrenheit to centigrade, the number is to be multiplied by 5 and divided by 9: but as the degrees do not in number start from the same point, the Fahrenheit scale being already 32° when the centigrade begins, it is necessary to add 32° to the number of Fahrenheit degrees which have been attained by calculation from the centigrade, and to subtract 32° from the number of degrees on Fahrenheit, which are to be converted into degrees upon the other scale.

Thus, to reduce 167° of Fahrenheit, we proceed:

$$167-32=135, \text{ and } 135\times\tfrac{5}{9}=75^\circ,$$

and find it to correspond to 75° centigrade. And to reduce 65° centigrade to Fahrenheit's scale, we say,

$$65\times\tfrac{9}{5}=117, \text{ and } 117+32=149^\circ,$$

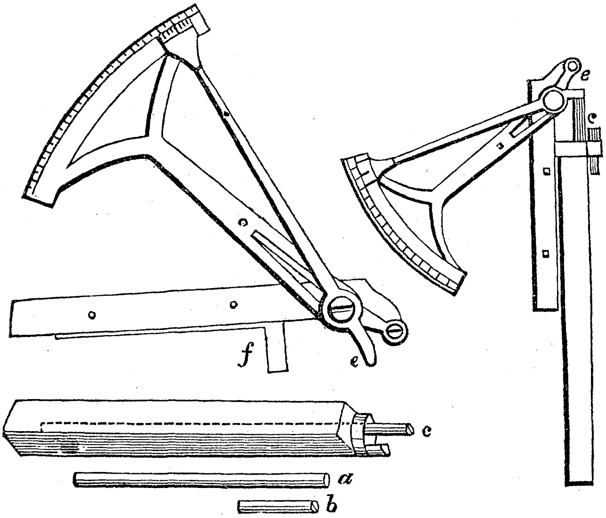
corresponding, therefore, to 149° of Fahrenheit.

Reaumur's scale being to the centigrade scale as 4 to 5, similar reductions are made to and from it, by using $\frac{4}{9}$ in place of $\frac{5}{9}$, as has been employed in the example.

The range of temperatures observable with a mercurial thermometer on Fahrenheit's scale is from —39° to +630°. The mercury freezes a little below —40°; and though it does not boil until it arrives at 660°, yet the quantity of vapour which it forms when very near its boiling point, prevents its indications from being quite exact between that point and 630°.

Our means of estimating temperatures above the boiling point of mercury are not at all so perfect as those that have been described for the lower degrees of heat. Mercury, when boiling, is not in the slightest degree luminous, but the temperature at which a heated body becomes visible in the dark, by emitting a dull red light, is not much higher. Numerous instruments have been invented for the purpose of determining the higher temperatures, particularly of furnaces, and hence they have been called pyrometers. Of these, the only one which appears to give accurate results, and hence deserves description, is that of Daniell.

In this pyrometer, the change of temperature is shown by the excess of the expansion of an iron bar over the expansion of a black-lead case in which it is enclosed. The iron rod *a* is somewhat shorter than the black-lead-ware case, and a plug of earthenware, *b*, which fits tight in the case, abuts against the iron rod inside, and projects as at *c* in the figure. Let us suppose the length of the case to be 5 inches, that of the iron rod $4\frac{1}{2}$ inches, and that of the earthenware plug to be 1 inch. If the whole be heated until the case shall have expanded by 12 parts, the iron rod will have increased in length by 44, and the earthenware piece by 7, which,



added to 44, makes 51. If the black-lead case did not increase in size, all these 51 parts should project; but as there is additional room made for 12, the projecting portion is only 39. If the parts of the apparatus were all free to move, each contracting again on cooling, the result would be that all would be restored to their original position; but this is not the case. The bar of iron, in expanding, pushes out before it the plug of earthenware, which, however, is held so tight in the case that it cannot go back again when the apparatus has become cold. The protrusion of the earthenware plug is therefore a permanent index of the greatest amount of expansion that had been produced while the instrument was exposed to heat. This expansion is, however, very small. The three pieces being, as stated, 5, $4\frac{1}{2}$, and 1 inch, the expansion, when heated from 32° to 212°, is only $\frac{39}{1000}$ of an inch; and as this indicates 180 degrees, the expansion for a degree is only about $\frac{1}{4500}$ of an inch. It is therefore necessary to magnify this expansion, in order that the indication may be read off; and this is done by means of a graduated circular arch, *d e f*, with a movable index, kept by means of a spring constantly at 0° when undisturbed. On fitting this scale to the pyrometric black-lead case, after it has been in the fire, the projection of the earthenware plug, *c*, catches in the prolonged heel of the index, *e*, and moving it round, the point of the index travels over a portion of the graduated scale, and indicates the number of degrees through which the temperature had been raised. This instrument is not always made of the same size, and hence the absolute amount of expansion may vary, which, however, is reduced to the same proportion on the scale, by which, also, the increase in the rate of expansion of the metallic bar at very high temperatures must be allowed for. By means of this very ingenious and useful instrument, Professor Daniell has determined the melting point of most of the important metals, and also several other temperatures at which remarkable phenomena occur.

The pyrometers of Wedgewood, of Guyton, and many others that have been proposed, must be considered as now totally abandoned, and do not require notice.

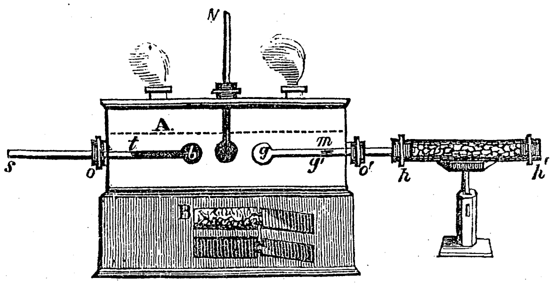
The most delicate, and perhaps the most important, measure of heat that has been contrived, is one totally independent of expansion, and founded on the measurement of an electric current which a change of temperature produces under certain circumstances. It is the *Thermo-multiplier* invented by Nobili. The principle which the instrument involves in its construction and its form will be described under the head of electricity, and the remarkable results obtained by means of it, and which have completely remodelled

our ideas of the physical constitution of heat, will be noticed in another place.

It may be of interest to subjoin the temperatures on Fahrenheit's scale at which some of the most remarkable effects of heat are produced:

— 135°. The greatest cold that has been produced.
— 121°. The solid compound of alcohol and carbonic acid melts.
— 91°. Greatest cold by ordinary freezing mixtures.
— 58°. Temperature of the planetary spaces.
— 60°. Greatest cold observed in the arctic regions.
— 47°. Sulphuric ether congeals.
— 45°. Nitric acid congeals.
— 39°. Mercury congeals.
+ 1°. Oil of vitriol freezes.
+ 14°. Oil of turpentine freezes.
+ 20°. Wine freezes.
+ 25°. Blood freezes.
+ 32°. Ice melts.
+ 36°. Olive oil freezes.
+ 98°. Heat of human blood.
+ 108°. Phosphorus melts.
+ 174°. Alcohol boils.
+ 201°. Rose's metal melts.
+ 211°. Newton's metal melts.
+ 212°. Water boils.
+ 218°. Sulphur melts.
+ 662°. Mercury boils.
+ 810°. Antimony melts.
+ 980°. Red heat.
+ 1141°. Heat of a common fire.
+ 1869°. Brass melts.
+ 1873°. Silver melts.
1996°. Copper melts.
2200°. Gold melts.
2786°. Cast iron melts.

The details which have been given, regarding the construction of the air thermometer, will show sufficiently the principle upon which the determination of the rate of expansion of gaseous bodies has been effected. The exact amount of dilatation was first ascertained by Dalton and Gay Lussac nearly at the same time. The apparatus of Gay Lussac consisted of a tin vessel, A, having five apertures.



By means of the aperture in the side, o', there is introduced the tube with the bulb,

$g\ g'$, containing air dried by the tube $h\ h'$, and arranged with the graduated scale and index globule of mercury m, as described in page 48. By the opposite orifice, o, is fixed a thermometer, $b\ s$, the bulb b of which is on the same level as the bulb of the air tube. By means of the central orifice in the top, a second thermometer, v, is introduced, the bulb of which is situated exactly in the centre of the box. The other orifices in the top are for the free escape of steam. The apparatus so being arranged, water, rendered ice-cold by some snow or ice floating on it, is introduced, until the thermometers and the air bulbs are covered to the depth of a couple of inches, and the index globule of mercury is thus brought to the zero of the scale. The box is then placed on a furnace, B, and gradually heated: the rise of temperature is indicated by the thermometer, t, the expansion by the motion of the index globule, and at each degree the thermometer and air bulb may be compared together until the water is brought to boil.

By substituting other substances for water, such as oil, or a bath of fusible metal, the rate of expansion may be determined for still higher temperatures, and has been thus ascertained by Dulong and Petit up to the boiling point of mercury.

From such experiments, conducted by Dalton, Gay Lussac, and Dulong, it resulted, that 1000 volumes of air, when heated from 32° to 212°, became 1375, and that the change was in proportion for higher or lower temperatures. The numbers actually obtained may be stated as in the following table:

Temperature on a Mercurial Thermometer by Fahrenheit's Scale.	10000 Volumes of Air at 32° become	Expansion for one Degree on F. Scale in Parts of the Volume at 32°.
— 33	8650	20·77
+ 32	10000	
212	13750	20·83
300	15576	20·70
387	17389	20·82
473	19189	20·84
559	20976	20·83
660	23125	20·90

The mean of these results gives the expansion for one degree at 20·81, or almost exactly $\frac{1}{480}$ of the volume at 32°, which result had been adopted universally, without any suspicion of its being imperfect. Circumstances having, however, induced Rudberg to submit the subject to an accurate reinvestigation, conducted with exceeding care and attention, particularly to the state of dryness of the air employed, he has found that the amount of expansion assigned by Gay Lussac and Dalton is somewhat too great, and that a volume of air, in being heated from 32° to 212°, expands from 1000 volumes to 1365.

The method which he employed was almost exactly the inverse of that of Gay Lussac. Having dried with great care the air in a glass bulb, the tube of which was drawn to a fine point, like that described, page 14, for taking the specific gravity of vapours, he heated it for a long time in a vessel of boiling water, taking care that all parts of the bulb and tube were equally heated, and then, being completely certain that all the air had attained the maximum temperature, he sealed, by the blowpipe, the minute orifice, and thus had the bulb containing air in the expanded state. The vessel being then removed to a trough of mercury, the orifice of the tube was placed deep below the surface, and carefully opened; a quantity of ice was then laid upon the globe, and being supplied as fast as it melted, the whole was thus left for some hours until the temperature was well established at 32°, and all the mercury which would rise into the globe by the contraction of the air by cooling, had entered. The height of the mercury was then noticed, and the height of the barometer, and the corrections necessary for its positive amount, or for any change which occurred during the experiment, allowed for, as already described. The volume of the mercury which had entered into the globe was then ascertained, and the volume of the globe itself also determined; and by a comparison of these, corrected for the expansion of the glass, and for any variation in the boiling point from 212°, the rate of expansion and its amount were calculated.

From very numerous experiments, Rudberg inferred that, in being heated from 32° to 212°, 1000 volumes of air became between 1364 and 1366·4; we may consider 1365, which is between the two, as

being absolutely the most correct, and hence that for each degree 1000 volumes expand $\frac{365}{180}=2{\cdot}028$, or $\frac{1}{493}$ of its volume at 32°.

In all operations upon gaseous mixtures, the rate of expansion of air comes into play; for as all gases expand alike, and the vapours, even of these bodies which are least volatile, as camphor and corrosive sublimate, expand, while in the elastic form, precisely as gases do, their volumes are corrected for temperature and pressure in the same manner. In determining the specific gravity of a vapour, it is also usual to reduce it to the same standard as those of gases, that is, air at 32°, even where the substance is of such a nature as that at 32° it may not produce any sensible vapour at all. In doing so, it is assumed that the vapour should, in cooling to 32°, follow the same law as common air; and hence an error, even though very slight, in the rate of expansion of air, might lead to incorrect results in many cases.

The application of such corrections follows very simply from what has been described. If there be a certain quantity, as 155 cubic inches of hydrogen gas at 142° Fahrenheit, and we wish to know the volume there should be when cooled to 32°, we say that, as 142° is 110° above 32°, the 155 cubic inches are equal to the volume at 32°, and in addition to $\frac{110}{493}$ of it; that being the quantity by which it is expanded from 32° to 142°. Therefore, denoting the volume at 32° by the letter V, there is the equation:

$$155=V+V\frac{110}{493},\text{ or }V=\frac{493\times155}{493+110}=129{\cdot}5:$$

129·5 cubic inches are therefore the volume at 32°.

If, on the other hand, we have a gas at a low temperature, and we wish to ascertain what its volume should be at 32°, it is evident that the mode is the same, except that, in place of subtracting the amount of expansion, we add it to the original volume. Thus, if the 155 cubic inches of hydrogen had been at 6° Fahrenheit, then the equation should have been 32°—6° being 26.

$$155=V-V\frac{26}{493},\text{ or }V=\frac{155\times493}{493-26}=168{\cdot}3\text{ cubic inches in exact numbers.}$$

It frequently happens that it is necessary to reduce a gas at one temperature to its volume at another, neither of which being 32°, it would require two different sums to be worked by the above process. But it may be effected as follows by a single calculation.

The volumes at the two temperatures are to one another in the same proportion as the standard volume, 493, increased by the amount of expansion proper to the temperatures. Thus, at the temperatures of 75° and 42°, the standard volume, which is 493°, at 32° becomes respectively 536 and 503. Now any volume of gas, when heated from 42° to 75°, or cooled from 75° to 42°, changes its volume in these proportions; and hence, if we have, for example, 127 cubic inches of a gas at 75°, and we wish to calculate its volume when at the temperature of 42°, we say, calling the unknown volume V:

$$V : 127 : : 503 : 536,\text{ and }V=\frac{127\times503}{536}=119{\cdot}2.$$

The formulæ for these corrections may be very simply written in a general form. thus, to reduce a volume to 32°, denoting the temperature on Fahrenheit's scale by t; by V, the volume of gas which we have measured at that temperature; and by V_1, the volume at 32°, the formula is:

$$V_1=\frac{493.\ V}{493\pm(t-32^\circ)}.$$

And to reduce, without reference to 32°; denoting the known volume by V, and the unknown by V_1; the temperature of V by t, and that of V_1 by t_1, there is found:

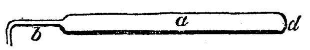
$$\frac{V_1}{V}=\frac{493\pm(t_1-32)}{493\pm(t-32)},\text{ and }V_1=V\frac{493\pm(t_1-32)}{493\mp(t-32)}.$$

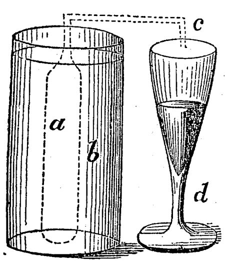
Air which has been heated becomes, from its great increase in volume, specifically much lighter than cold air, in which it therefore ascends with a velocity due to the difference between their

specific gravities. It is thus that over every lamp or candle there may be felt a current of heated air ascending from the flame; that the heavy dark smoke rises in its heated form from the chimneys of our houses; and that, in crowded apartments or theatres, the upper portion of the space will be occupied by oppressively hot air, while that near the floor will be quite cool. By the ascent of the heated air from our furnaces and fireplaces, there is generated the draught which gives the supply of air necessary for continued burning; and as the intensity of the combustion and consequent heat produced depends on the rapidity of draught, the hot air is kept from being cooled by mixing with the cold external air, by being collected in the chimney, where it obtains an ascensional power corresponding to its height, and by which we are enabled to regulate with accuracy the temperature which shall be produced. On this ascensional power of heated air is founded also the construction of the fire or Montgolfier balloon, a bag of hot air, rising in the surrounding colder atmosphere, precisely as a light flask, filled with oil or alcohol, would ascend if let loose at the bottom of a vessel full of water.

It has been already noticed that liquids do not, in expanding, follow any simple proportion, such as that which exists for gaseous bodies, but that each fluid has a peculiar dilatability of its own, and that the rate of expansion varies with the temperature, being greater in the higher portion of the thermometric scale than in the lower. Liquids expand much less than gases, but much more than solids; for, as is particularly instanced in the thermometer, the visible expansion of a fluid is, in most cases, only the excess of its expansion over the expansion of the solid vessel in which it may be contained.

To measure the amount of expansion in liquids, they may be introduced into graduated thermometer tubes; and then, when exposed to the same degree of heat, they will indicate temperatures proportional to their expansibilities. Thus alcohol rising more into the stem than water, and water more than mercury, will stand at different marks on the stem, although the temperature be really the same. It may, however, be more easily and more accurately done by means of the apparatus in the figures. *a d b* is a glass tube, the neck of which is very narrow, and bent as in either figure. This tube is to be filled completely, at the lowest temperature, with the liquid, whose expansion is to be examined and then weighed, the weight of the tube itself being previously known, and the quantity of liquid which it contains is thus determined. The tube is to be then placed upright in a cylinder of water or oil *b*, to which heat may be applied by a furnace below; and the liquid expanding according as its temperature is raised, the excess of volume flows out at the capillary beak *c*, and may be collected as in *d*, or let to waste. When the apparatus has been brought to the highest temperature required, and all farther expansion has ceased, as is known by no more liquid passing out at *c*, the tube is to be removed from the bath, carefully cleaned, and, when again cool, accurately weighed. The loss of weight is the quantity of liquid that had been expelled, and this, compared with the whole original quantity of liquid, gives the proportion of expansion. In this manner, however, the result appears to be less than it really is, for the expansion of the glass tube itself diminishes the quantity of liquid expelled. Such results require, therefore, to be corrected for the expansion of the glass, which is, however, so small, that in the more dilatable liquids it may be neglected. In mercury, however, it affects the apparent expansion very much: mercury expanding in glass through 180°, augments in volume only $\frac{1}{67}$, while its real expansion is $\frac{1}{55}$

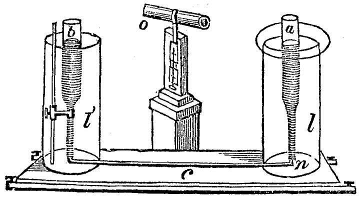




The amount of expansion of different fluids in passing through 180° of Fahrenheit is thus found to be:

Alcohol	$\frac{1}{9}$	Oil of turpentine	$\frac{1}{14}$
Nitric acid	$\frac{1}{9}$	Sulphuric acid	$\frac{1}{17}$
Fixed oils	$\frac{1}{12}$	Water	$\frac{1}{23}$
Sulphuric ether	$\frac{1}{14}$	Mercury	$\frac{1}{55}$

The actual amount of expansion, independent of the expansion of the containing vessel, is best observed by the apparatus used by Dulong and Petit. It consists of



a glass tube *a b c*, bent in the form of a U, of which the horizontal portion *c* is narrow, but the vertical legs pretty wide. When mercury is poured into the tube, it stands at the same height in both legs if the temperature be the same; but one leg being immersed in a vessel of oil or water *l*, by which heat can be applied to it, and thereby the mercury in it caused to expand, the height of the liquid column must increase in order to balance the colder column of mercury in the proportion of the augmented volume. The difference between the heights being read off, by means of an accurate scale, with a telescope *o*, the amount of absolute expansion may be easily calculated from it.

By means of this instrument Dulong and Petit determined the rate at which the expansion of mercury increases with the temperature, as has been noticed generally in the description of the thermometer. Their result was, that between 32° and 212°, measured on the air thermometer, the expansion is $\frac{1}{55\cdot5}$. From 212° to 392°, it is $\frac{1}{54\cdot25}$; and from 392° to 572°, it is $\frac{1}{53\cdot00}$. The consequence is, that, measured by its own expansion, mercury boils at 680° Fahrenheit; but from the expansion of the glass of an ordinary thermometer bulb, it boils at 660° on the visible scale, which coincides almost exactly with 662°, the temperature given by the dilatation of air. The apparent expansion of mercury in glass is therefore taken as being uniform for 180°. $\frac{1}{67}$ of its volume.

Considerable simplicity is given to the laws of dilatation of liquids by an observation of Gay Lussac, that, in order to obtain any common rule for them, such as is found for gaseous bodies, we must examine them when in the same molecular condition; that is to say, the cohesive powers of the liquids we employ must be brought into the same state. This is most nearly done by taking these liquids when heated to their boiling points, for then the cohesion of each liquid is about to cease altogether. Thus alcohol boils at 173°, water at 212°, sulphuret of carbon at 134°, and sulphuric ether at 96·3°; and, taking 1·000 volumes of each at their boiling points, and allowing them to cool, they contract as follows:

By cooling through	Water contracts	Alcohol contracts	Sulphuret of Carbon contracts	Ether contracts
18°	6·61	11·43	12·01	16·17
36°	13·15	24·34	23·80	31·83
54°	18·85	34·74	35·06	46·42
72°	24·10	45·68	45·77	58·77
90°	28·56	56·02	56·28	72·01
108°	32·42	65·96	66·21	....

We by this means find a very interesting relation between alcohol and sulphuret of carbon, two fluids remarkably different in their specific gravities, and in their chemical constitution and properties. It appears that their molecular force must increase at the same rate; for in cooling the same number of degrees below their boiling points, they contract to exactly the same amount: and a still farther connexion is exhibited between their molecular conditions by the remarkable fact that, in being converted into vapour, the augmentation of volume which they undergo is the same.

Many liquids possess the property of contracting, by reduction of temperature, only to a certain point; below which, if the cooling be continued, they expand. As the volume at this temperature is the least possible, it is called the point of maximum density. This peculiarity was first recognised in water; but it has since been

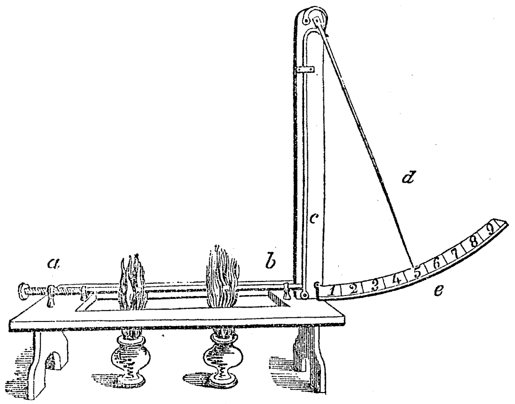
found in many other fluids, even in a still more remarkable degree It is, however, in water that the phenomenon is of most importance, in consequence of the extensive agency of that fluid in natural operations. The point of maximum density of water has been determined by the experiments of very many persons to be 39.5° of Fahrenheit. When water below that temperature is heated, it contracts; when heated above it, it expands: when cooled from above it, it contracts; when cooled below it, it expands: and when the experiment is made in glass vessels, the contraction of the glass has the effect of rendering the expansion of cooling below, or of heating above, through the same number of degrees, exactly equal. Thus 100·000 volumes of water become 100·012 equally by being cooled from 39·5 to 32°, or by being heated from 39·5 to 46°, and the specific gravity of water at 46° and at 32° is consequently the same.

A great deal of the permanence of the existing order of nature depends upon this property of water: it is by means of it that the great mass of water in our lakes and rivers is preserved from being converted into solid ice. When, by the cooling process of the winds, the water has been all reduced to the temperature of 39·5°, the surface acts as a screen to prevent the farther loss of heat, and thus retains the deeper portions at a temperature sufficiently high for the existence of its organized inhabitants; for, by the continued action of the cold wind, the superficial water being cooled below 39·5°, it becomes lighter, and floats upon the heavier and warmer water underneath; and from the bad conducting power which water will be hereafter demonstrated to possess, the loss of heat is effectually prevented. If it were not for this property of water, all large collections of it in lakes and rivers would, with few exceptions, be permanently frozen.

The dilatation of solids is much inferior in amount to that of liquids, and as with these, the rate of dilatation is not uniform, but increases with the temperature. The increase is, however, so exceedingly minute, that in almost all cases it may be neglected, and hence need not occupy much attention. The dilatation of solids, although so small, may yet be demonstrated to be real by many simple experiments. Thus, if an iron rod be made to fit, when cold, in length and breadth, an exact scale, it will be found, when heated, to be too large to enter it. An iron ring, which is, when cold, too small to pass over a cylinder, becomes sufficiently large on being heated; and if the cylinder could have passed through when cold, its diameter becomes too great to allow its passage when its temperature is raised. In the arts, the expansion of solids, particularly of the metals, in this way becomes the source of numerous inconveniences, and of many useful applications. Thus, the iron rim of a carriage wheel is secured by the power of its own contraction, it having been slipped upon the wooden frame while in a hot and expanded state. The force of contraction of iron bars in cooling has been applied successfully to restore to the proper position buildings which had been about to fall, and the rate of expansion has also, as in the pyrometers of Daniell and others, served as a useful measure of high temperatures; on the other hand, by the alternate expansions and contractions, under the successive influence of win-

ters and summers, of the metallic bars which had imprudently been laid in the masonry of some important public buildings, with the idea of giving additional security, the courses of stone or brick have been loosened from one another, and reconstruction rendered necessary, in order to prevent their being gradually pulled to pieces.

In estimating the amount of expansion of a solid body, the great difficulty is the accurate measurement of the small increase in length which takes place. For this purpose, a great variety of mechanical arrangements have been constructed. As they are all in principle the same, and the detailed description of any exact form would occupy too much space, it will be sufficient to notice one, which, though not that by which very accurate numbers may be obtained, is calculated to give a very satisfactory idea of their general construction: *a b* is the bar of which the expansion is to be determined; it is fastened securely at the extremity *a*, and rests at *b* in a groove along which it is free to move, as in the figure. This end of the bar at *b* presses against a rod *c*, which is a lever of the second order, very near the fulcrum, and this transfers its motion to the end of the lever, increased in the proportion of the distance.



This lever acts on another similar one, *d*, the extremity of which serves as an index on the graduated circular arc *e*, by which the amount of expansion is read off. Thus, if the acting lengths of the arms of the levers are respectively 1 and 20, and the end of the bar *a* at *b* moves $\frac{1}{1000}$ of an inch, the end of the index *d* will move on the scale *e* through $\frac{20 \times 20}{1000} = \frac{4}{10}$ of an inch, a space capable of being divided by a microscope and vernier into 200 measurable spaces, so that an expansion of the two hundred thousandth of an inch can be accurately determined. For a popular illustration, the source of heat may be lamps, as in the figure; but for accurate experiments, the bar is completely immersed in a bath of oil or water, and the temperature ascertained by a suitable arrangement of thermometers.

The most important results thus obtained are the following. The temperature being raised from 32° to 212°, the increase in length of a bar of

Glass varies from	$\frac{1}{1284}$	Steel	$\frac{1}{926}$
to	$\frac{1}{1090}$	Gold	$\frac{1}{661}$
Copper	$\frac{1}{582}$	Silver	$\frac{1}{524}$
Brass	$\frac{1}{532}$	Lead	$\frac{1}{351}$
Soft iron	$\frac{1}{815}$	Tin	$\frac{1}{462}$

The increase in length is called the linear dilatation of a sub

stance, but its increase of volume is called the cubical dilatation, and is three times the former. Thus the cubical dilatation of glass is $\frac{3}{1284}$, or $\frac{1}{428}$. Hence a glass ball which holds 428 measures at 32°, becomes capable of holding 429 at 212°; or if it hold 10·000 at 32°, it holds 10·023 at 212°. In this manner the correction for the expansion of glass is in all cases made. But it is necessary to apply the amount of expansion belonging to the particular sort of glass; thus, in the account of the thermometer in page 51, the cubic dilatation of glass was taken, not as 10·023, but 10·026.

[The reason that the cubic dilatation may be taken as equal to three times the linear, without sensible error, is due to the circumstance that the linear dilatation is always a small fraction of the primitive length. If $1+l$ represent the dilated length, $(1+l)^3$, or $1+3\,l+3\,l^2+l^3$ will be the true volume; but as l is a small fraction, its triple square and cube may be neglected.]

Although it is abundantly proved that solid bodies expand more rapidly at high than at low temperatures, yet, except in the case of some particular substances, as glass, iron, and platinum, whose utility as measurers of heat rendered a knowledge of the law of their expansion necessary, the subject has been little examined; the degree to which the rate of expansion is affected by temperature will be sufficiently shown in the table which follows. At the temperature of 212° Fahrenheit, as given by an air thermometer, the dilatation for one degree is thus, for

Glass.	Platinum.	Iron.	Copper.
$\frac{1}{59660}$	$\frac{1}{67860}$	$\frac{1}{50760}$	$\frac{1}{34120}$

while at 572° of Fahrenheit it becomes, for

Glass.	Platinum.	Iron.	Copper
$\frac{1}{59220}$	$\frac{1}{65340}$	$\frac{1}{40678}$	$\frac{1}{31860}$

and the temperature deducible from the expansion of a thermometer made of each of these substances should be, in passing from 212° to 572°, as compared with air,

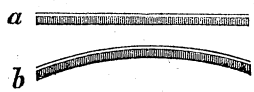
Air.	Glass.	Platinum.	Iron.	Copper.
572°	667°	592°	702°	623°

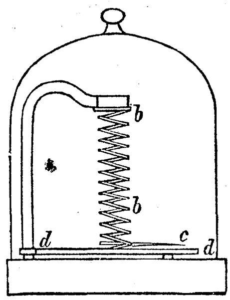
Platinum expands thus the most regularly of those bodies, and should, therefore, be best fitted for a metallic thermometer.

It is remarkable that the rate of expansion is not increased by rise of temperature for all solid bodies, but, on the contrary, in some cases there exists, for solids as for liquids, a point of maximum density, so that the body shall expand whether it be cooled or heated from that degree. This is peculiarly the case in Rose's fusible metal, which has been so often mentioned as a means of applying a steady heat. When heated from 32° to 111°, this metallic alloy increases in volume from 100·000 to 100·830 parts, but there the expansion stops, and when farther heated it contracts, until, when at 156°, the volume is only 99·291, being less than at 32° By a farther rise of temperature it again expands, and at 178° is at its original volume of 100·000, and continues expanding until, being 100·862 at 201°, almost exactly what it had been at 111°, it begins to melt. It is curious that it has no point of maximum density when in the liquid state.

The different rates of expansion of different solid bodies are subservient to some very important uses in the arts and in scientific research. Thus, the difference between the expansibilities of platinum and brass, or any other two metals which differ much, may be used as a very delicate thermometric means. If we take a flat rule

of platinum exactly ten inches long at 32°, and lay it on a similar rule of brass, to which it is firmly screwed at one extremity, and on which, at the free end, there is engraved a scale of parts of an inch for a small space, the compound rule will serve as a thermometer. For the two rules being exactly of the same length at 32°, if we place them, fastened together, in boiling water, the brass rule will be elongated by 0·019, while the platina rule will expand only through 0·009; hence the end of the brass rule will project beyond the platina rule by 0·010 of an inch; and as the expansion is uniform for these moderate temperatures, each degree of Fahrenheit's scale will be indicated on the scale of the brass rule by $\frac{0\cdot010}{180}=\frac{1}{18\,000}$ of an inch. In this form the spaces would be too minute to be easily determined; but by modifying the form, and connecting the rules through their whole length, the beautiful metallic thermometer of Breguet has been invented. Its principle is as follows: if the two rules be soldered completely together, as in *a*, in place of being connected only at a single point, the result of the unequal expansion is to bend the bar, as in *b*, until, the most expansible metal being on the outside, it forms an arch longer than that formed by the inside rule, by the difference of their expansions. If the compound bar be already bent into a circle, the ends of which are not opposed, the effect of the expansion is to make these edges project, and to diminish the diameter of the circle; by having a number of such circles, the expansion of all being added together, a considerable circular motion is produced in the extremity. In the thermometer of Breguet there is such a compound spiral *b*, *b*, fastened at the upper end, and having attached to its lower extremity an index, *c*, which moves round a dial, *d*, *d*, and indicates the temperature of the instrument. On this relative expansion is also founded the construction of the compound pendulum. A metallic bar, when used, as in an ordinary clock, to measure time by its vibrations, being constantly changing in length according as the external temperature varies, affects the rate of the clock, making it go too fast or too slow by its shortening or elongation. This is corrected by having two or more bars, by the expansion of one of which the vibrating length of the pendulum is increased, while by the expansion of the other it is just as much shortened; the consequence of this opposing action is, that the pendulum remains indifferent to all changes of temperature, and the clock becomes an exact measure of time at all seasons.





SECTION II.

OF SPECIFIC HEAT.

It is now necessary to examine into the quantity of heat which each substance requires to raise its temperature a certain number of degrees; for, although it be quite impossible to assign the absolute

proportion, yet, by obtaining the relative proportions, we may arrive at results which may serve to characterize those substances, and may, as shall be hereafter shown, lead us to important views of the relations between their physical and chemical constitution. The relative quantity of heat necessary to raise the temperature of any body through a certain number of degrees, as ten, for example, is termed its *specific heat.*

If we take a pint of water at 150°, and another pint of water at 50°, and mix them well in a very thin vessel, the temperature of the mixture is found to be, if we allow for some sources of error to which this process is exposed, exactly 100°. Thus the one part of the water has transferred to the other a quantity of heat sufficient to raise its temperature 50°; and whether this addition was from 50° to 100°, or from 100° to 150°, the result was the same. In water, therefore, the specific heat does not change within these limits; but it will be found that in high temperatures a trifling increase does occur; for the present purpose, however, it may be neglected. If, now, a pint of water be taken at 150° as before, and a pint of mercury at 50°, and they be well and rapidly mixed together until both have attained the same temperature, this will be found to be 118°. The mercury here rises from 50° to 118°, through 68°, while the water cools only through 32°, or not quite half as much, so that the same quantity of heat can raise the temperature of mercury through twice as many degrees as that of water.

Taking thus equal volumes, the specific heats of water and mercury are as 68 : 32; or water being adopted as the standard for liquid and solid bodies, and its specific heat taken as 1, the specific heat of mercury is 0·47 nearly. Such bodies are, however, generally taken, not in equal volumes, but in equal weights, and hence it is necessary to divide the 0·47 by 13·5, the specific gravity of mercury, and thus there is obtained 0·035, its specific heat.

The process now given is known as the method of mixtures, and has been selected for example, as that by which the meaning of the term specific heat is best explained; but it is not the only one, nor even, perhaps, the best, by which specific heat may be determined. The sources of error are, that a certain quantity of heat is absorbed by the vessel in which the mixture is made, and that, as the mixture requires some time to make, a certain loss occurs by the cooling power of the air. But it is, however, in skilful hands, capable of exceeding accuracy; and, with the recent improvements that have been made in its details by Regnault, it has yielded results of the highest value to science. The various forms of apparatus used in such experiments need not be described. For the use of the method of mixtures, it is not necessary that the two bodies should be liquid. Thus, if a pound of pure copper in a bar be heated in an oil bath to 300°, and be then immersed in a pound of water at 50°, the copper will give out its excess of heat to the water, and both will arrive at a temperature of 72°. The copper has therefore lost 228°, and the water has gained 22°, and the specific heats being inversely as these numbers, that of copper is found thus to be $\frac{22}{228}=0{\cdot}096$, water being 1·000.

One process employed by Dulong and Petit consisted in heating

to the same degree the bodies to be tried, and allowing them to cool exactly under the same circumstances. It is evident that, if we know exactly the rate at which a body cools, and the time which it takes to cool, we can calculate exactly how much heat it parts with. Thus, if we have two bodies heated to 300°, and circumstanced in all respects alike, one requires 15 minutes to cool to 50°, and the other 25, the latter will have parted with more heat, in the proportion of 25 to 15, and the specific heat is expressed by the quantity of heat the body gives out in cooling. Hence those substances which have high specific heats require more time to heat or cool, through a certain number of degrees, than those bodies whose specific heat is less.

It was by a process of this kind that the relative specific heats of bodies was first discovered. Boerhaave having remarked that, when two thin glass vessels, containing, one a pound of water and the other a pound of mercury, were equally exposed to the heat at the front of a strong fire, the temperature of the mercury rose much more rapidly than that of the water, and that it attained its greatest degree in one half of the time which the water required; and also, when both, equally hot, were removed from the fire, the mercury cooled twice as fast. For accurate purposes, however, there are many precautions necessary in order to place the substances under the same conditions, so as to render the rapidity of cooling depend ant only on their different specific heats; thus, equal weights of the different bodies are placed in the same thin polished silver vessel, so that their external surface may be the same in extent and nature, and this vessel cools in an exhausted receiver in order that there may be no loss of heat from contact with the external air. The internal surface of the receiver must also be always in the same state, that the heat given out may pass off in all cases with equal facility.

An extensive series of researches on the specific heats of bodies, conducted by the illustrious associates Lavoisier and Laplace, has been found on repetition to have been rendered useless by the imperfections of the apparatus they employed: it was termed the Calorimeter, and consisted of a vessel containing ice, in the centre of which the heated body was placed, and the quantity of heat this gave out in cooling was measured by the quantity of ice which was melted into water. Outside there was another case of ice to defend the instrument from the action of the air. It was found in practice impossible to collect all the water. A quantity remained infiltrated among the ice, some solidified in one part of the vessel after having been melted in another, and, consequently, the numbers given by two of the greatest men that have ever been attached to science must be considered as quite without authority. In cases, however, where the quantity of heat was very large, as when the Calorimeter was employed to determine the quantity of heat produced in combustion, these sources of error became less influential, and such results will be utilized in a future chapter.

The specific heats of a number of the most important solid and liquid bodies, determined by such methods, are given in the following table:

Water	=1·000	Iron	=0·114
Ether	=0·520	Copper	=0·095
Alcohol	=0·660	Lead	=0·031
Sulphuric acid	=0·333	Gold	=0·032
Nitric acid	=0·442	Antimony	=0·051
Sulphur	=0·202	Tin	=0·056
Carbon	=0·241	Iodine	=0·054
Mercury	=0·033	Phosphorus	=0·188

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Arsenic . . . . . . =0·081	Glass . . . . =0·177
Platinum . . . . . =0·032	Calomel . . . . . . =0·041
Silver . . . . =0·057	Common salt . . . =0·225
Zinc . . . . =0·095	Nitrate of soda . . . =0·240
Tellurium . . . . . =0·051	Lime . . . . =0·205
Nickel . . . . =0·109	Magnesia . . . . . . =0·276
Cobalt . . . . =0·107	

The numbers given are generally those lately obtained by Regnault.

The specific heats of bodies are not the same at all temperatures; thus Dulong and Petit have found that the specific heats, calculated from the change of temperature from 32° to 212°, and from 32° to 572°, differ, as in the following table:

Substance.	Sp. Heat from 32° to 212°.	Sp. Heat from 32° to 572°.
Mercury	0·0330	0·0350
Zinc	0·0927	0·1015
Antimony . . .	0·0507	0·0549
Silver	0·0557	0·0611
Copper	0·0949	0·1013
Platinum . . .	0·0355	0·0397
Glass	0·1770	0·1900
Iron	0·1098	0·1218

The specific heat increases, therefore, with the temperature, and Nauman and Regnault have found that this holds, even with water; for, according to their experiments, the specific heat of water at 32° being 1·000, that water at 212° is 1·010, consequently the equal distribution of heat between warm and cold water, which was described at the commencement of this section, does not exactly hold; the temperature of the mixture should be a very little above the mean. This was, however, omitted, in order not to complicate the account of that manner of finding the specific heats.

The specific heats of bodies are connected very intimately with their chemical and molecular constitution, although we are not yet able to trace the exact cause of this connexion in all its forms. The discovery of such connexion was the most remarkable result of the experiments of Dulong, and it may be expressed as follows. If we take the specific heats of any of the bodies given in the table, and divide by each of them the number 3·1, we obtain a series of numbers which are found to be either those which shall be hereafter described as the chemical equivalents of the bodies, or to stand in some remarkably simple relation to those equivalents, thus:

Substance.	Sp. Heat.	$\frac{3·1}{\text{Sp. Heat.}}$	True Equivalent.
Lead	0·031	100·0	103·6
Tin	0·056	55·4	57·9
Zinc	0·095	32·6	32·3
Bismuth	0·030	100·7	71·0
Carbon	0·24	12·9	6·1
Iodine	0·054	57·4	126·3
Phosphorus . .	0·188	16·5	31·4
Silver	0·057	54·4	108·

In the first division of this table, the quotient is so close to the true equivalent as sufficiently to show that, were it not for the un

avoidable errors of experiment, they would coincide. In bismuth the result is $1\frac{1}{2}$ times the true equivalent. In carbon it is double the true equivalent. In iodine, in phosphorus, and in silver, it is one half. Each of these illustrations might be much extended, their numbers being only intended as examples of the fact.

The above are all simple bodies; but Nauman and Avogadro have shown, that also in compound bodies this connexion between the equivalent number and the specific heat exists, although the connecting dividend is no longer 3·1, but is a different number for each class of bodies.

Thus, for the following carbonates, the specific heats being made the divisors of the number 10·4, there is—

Substances.	Sp. Heat.	$\frac{10 \cdot 4}{\text{Sp. Heat.}}$	True Equivalent.
Carbonate of lime . .	0·2044	50·9	50·6
Carbonate of iron . .	0·1819	57·2	58·1
Carbonate of zinc . .	0·1712	60·7	62·4
Magnesian limestone .	0·2161	48·1	46·7

For certain sulphates the number is 12·4 Thus:

Substances.	Sp. Heat.	$\frac{12 \cdot 4}{\text{Sp. Heat.}}$	Equivalent.
Sulphate of barytes .	0·1068	116·1	116·1
Sulphate of strontia .	0·1300	95·4	91·9
Sulphate of lime . . .	0·1854	66·8	68·6

For a number of metallic oxides, the constant appears to be 5·4 Thus:

Substances.	Sp. Heat.	$\frac{5 \cdot 4}{\text{Sp. Heat.}}$	Equivalent.
Magnesia	0·276	19.6	20·7
Red oxide of mercury	0·049	110·2	109·4
Oxide of zinc . . .	0·132	40.9	40·3
Oxide of copper . .	0·137	39·4	39·6

The relation between the specific heats of bodies and their chemical equivalents is thus remarkably shown to extend not merely to the simple substances, but even to saline bodies, and indicates a connexion between the chemical equivalents and the molecules upon which the heat exerts its action, of an intimate description. In fact, the specific heat of a certain weight of any body is thus shown to be proportional to the number of chemically equivalent masses contained in that weight; and the constant numbers, which were divided by the specific heats, are the specific heats of the ultimate chemically equivalent particles. Thus, the specific heat of chemical molecules of zinc, of lead, and tin, is 3·1; that of the oxides of zinc, of copper, and of mercury, 5·4; the specific heat of the chemical atom or ultimate particle of carbonate of lime or of zinc, 10·4; and that of the sulphates of barytes, strontia, and lime, 12·4 Attempts have been made to connect these constants together, but without good foundation; for 5·4 and 12·4, although nearly the double and quadruple of 3·1, are yet too far removed to show any necessary connexion, and 10·4 is completely out of the series of 3·1, though nearly the double of 5·4.

I shall have occasion to discuss this remarkable relation between the physical and

chemical characters of these bodies when I come to examine the subject of the laws of chemical combination in their full extent. For the present, the details now given are sufficient.

It is not likely that any law connecting the specific heats of different bodies can be obtained perfectly consistent, for the various bodies necessary cannot be examined exactly in the same state Regnault has well observed, that the quantity of heat which we measure as specific heat consists of several different portions: 1st, the true specific heat; 2d, the heat which produces dilatation; 3d, the heat which causes the rise of temperature; and, 4th, when a solid is near its fusing point, the quantity employed in giving the softness and ductility, which most bodies at certain temperatures acquire. These last three portions being very small, do not conceal the law by which the true specific heat is regulated; but they influence it so far as to prevent the law from being verified in its numerical results with the accuracy which otherwise might have been obtained.

When bodies combine chemically, there is generally found to be a diminution of specific heat; and it has been attempted to account thereby for the rise of temperature, by which combination is in most cases accompanied. Thus, the specific heat of sulphuric acid is 0·33; and when mixed with an equal weight of water, the specific heat of the mixtures should be, were there no action, $\frac{1\cdot33}{2}=0{,}665$; but the true specific heat of the combined acid and water is found to be only 0·587. The excess, therefore, $0\cdot665-0\cdot587=0\cdot078$, becomes free, and shows itself by raising the temperature of the mixture; and, accordingly, on mixing together sulphuric acid and water, it is well known that a temperature higher than that of boiling water may be produced. It was even supposed at one time, when heat was looked upon as being a positive substance which combined with bodies in different proportions, that the absolute quantity of heat which a body contained might be determined by such an experiment, thus: if the rise of temperature produced by 0.078 of heat becoming free is expressed by 180° above 32°, then the quantity of heat which stays behind must be greater than that in the proportion of 587 to 78; and hence is equivalent to $\frac{587}{78}\ 180=1335°$: and thus, at the temperature of —1303° of Fahrenheit's scale, a body should contain no heat at all; it should be the absolute zero. But no two such experiments, with different bodies, ever gave the same result: and it is evident, from the fact of the specific heat diminishing as the temperature sinks, that the term at which the two quantities should vanish must be infinitely remote, and that there is no such thing as an absolute zero at all. In fact, the physical existence of an absolute zero is inconsistent with the more accurate ideas of the nature of heat, which modern investigation has suggested.

The development of heat, in chemical combination, is also only in some cases accompanied by a diminution of specific heat; in at least as many it is, on the contrary, remarkably augmented.

The specific heat of gases and vapours has obtained considerable attention; and yet, from the extreme delicacy of the processes necessary, and the small quantity of material which can be operated on, the results hitherto obtained have not acquired that degree of posi-

tive accordance which should render repetition unnecessary. The principal experimenters in this department have been Delaroche and Berard, Delarive and Marcet, Haycraft, Dulong, and, latterly, Apjohn and Suerman.

The method adopted by Haycraft, and by Delaroche and Berard, consisted in heating a quantity of gas to a certain temperature, and then, by passing it through a tube in a vessel of water, determining how much it raised the temperature of the water in being cooled through a certain number of degrees. In principle, this mode is perfect; but the extreme accuracy necessary in the management of the apparatus does not appear to have been attained by Haycraft: and Delaroche and Berard deprived their results of most of their value by the oversight of using the gases in a damp state. The process of Delarive and Marcet was not such as could lead to results worthy of much confidence. A glass globe full of gas, to which was attached a thermometer, with the bulb exactly in the centre, was plunged into a vessel of hot water, in the expectation that the time occupied by each gas, in having its temperature raised a certain number of degrees, would be proportional to the specific heat under a constant volume. But the communication of the heat would be so much and so variously affected by currents, according to the density of the gas and the quantity of heat absorbed by the gas, so trifling in comparison to that which would be required to heat the globe, that the amount of liability to error was very great.

The process employed by Dulong was very beautiful in principle, and calculated to give experimental results of great accuracy. It consisted in determining the velocity of sound in each gas, which was measured by finding the note the same organ-pipe gave with each: from this, by very ingenious methods, which, however, need not here be introduced, farther than that the gases with higher specific heats give more acute tones, he calculated the specific heats. The calculations were, however, based on certain other principles, which are not necessarily true.

The method contrived by Apjohn is that which appears to be the best calculated to give accurate results, and those which he obtained have been verified by the experiments of Suerman.

Apjohn's method cannot be completely described until we come to speak of the latent heat of vapours and their relation to space; but the general principle of it is, that if several gases be employed to convert a certain quantity of water into vapour, the gases will be cooled thereby in inverse proportion to their specific heats. Thus, if one gas have double the specific heat of another, it will saturate itself with vapour by cooling through only half the number of degrees necessary for that with the less specific heat; and thus, by measuring simply the cooling power of each gas, the specific heat may be calculated.

The numbers obtained by Delaroche and Berard, by Dulong and by Apjohn, for the specific heats of the gases in equal volumes, are given in the following table:

Gases.	Apjohn.	Delaroche.	Dulong.
Air	1·000	1·000	1·000
Nitrogen	1·048	1·006	1·000
Oxygen	·808	·976	1·000
Hydrogen	1·459	·900	1·300
Carbonic acid . . .	1·195	1·258	1·172
Carbonic oxide . . .	·996	1·034	1·000
Nitrous oxide . . .	1·193	1·350	1·159

These numbers show the diversity which exists among even the best experimenters; and they also show that the different gases follow no simple law regarding their specific heats. The principle laid down by Haycraft, Delarive, and Marcet, that in equal volumes all gases have the same specific heat, is thus shown, by the combined evidence of all the best results, to be totally unfounded.

It is sometimes necessary to compare the specific heats of gases with that of water; this being 1·000, that of air is 0·267 for equal weights, and so on for the other gases in proportion.

We do not know the specific heats of many bodies in the state of vapour. For watery vapour, however, it is found to be 0·847, water being 1·000, or 3·172, air being 1·000, for equal weights. Water is thus the only substance of which we know the specific heat in the three states of aggregation, that of ice being ·900, water 1·000, and steam ·847, for equal weights.

When the volume of a gas or of a vapour increases, its specific heat increases also, and *vice versa.* Hence, when air is suddenly condensed, so much heat is evolved that tinder may be lighted, and the barrel of a condensing syringe may become too hot to hold; thus, also, in some kinds of machinery where air suddenly expands, so great a degree of cold is produced that water may be frozen.

The exact degree of connexion between the amount of expansion of the gas and the increase, or of condensation and the diminution of specific heat, has not been ascertained. They are not proportional; that is to say, when the volume of a gas is doubled, its specific heat is not doubled, and *vice versa;* and yet it would appear that it does not fall much below that ratio.

SECTION III.

OF LIQUEFACTION.

It has already been frequently explained, that by the application of heat to a solid body, it commences, when its temperature has risen to a certain degree, to become liquid, and that this point, the melting point of such solid body, is one of the most determinate and characteristic of its physical properties. Accordingly, the melting point is often used as a means of distinguishing and recognising substances otherwise very similar in properties; as, for example, the numerous fatty acids can scarcely be otherwise distinguished from each other, exclusive of analysis, than by the temperatures at which they melt. There has been already given a list of the melting points of a number of solid bodies, and, in the history of each individual substance, its fusibility will be described.

The change from the solid to the liquid state is accompanied, however, by a phenomenon differing from any yet described, and deserving of great attention from the important consequences which flow from it. It is, that at the moment of liquefaction a very large quantity of heat is absorbed, combining, as it were, with the solid to form the liquid body, and after combination being insensible to the thermometer, and having thence obtained the name of *latent heat.* A pound of water at 32° and a pound of ice at 32° give on the thermometer precisely the same degree, and yet, independent of all considerations of specific heat discussed in the last section, and which we now lay aside, the water contains, in a state of intimate

combination, a great quantity of heat, by virtue of which it is liquid water, and by losing which it would be reduced to the state of solid ice. In melting, therefore, every body renders latent a quantity of heat.

This principle may be demonstrated by experiments of a very simple kind. Thus, if a pound of ice be taken at 32°, and added to a pound of water at 172°, the ice dissolves immediately, but the temperature of the resulting two pounds of water is found to be 32° There has thus disappeared a quantity of heat, which had previously raised the temperature of the water to 172°, or through 140°. This heat has been absorbed by the ice in becoming liquid, and rendered latent; and it is therefore said that the latent heat of liquid water is 140°. If a vessel of water, at the temperature of 52°, be exposed freely to air below the freezing point, it will rapidly cool until it arrives at 32°, but there the lowering of the temperature ceases; it begins to freeze, and, until the entire mass is reduced to solid ice, no loss of heat sensible to the thermometer is observed: yet it must still be giving out heat precisely as it was when it cooled from 52° to 32°, this heat being, however, that which gave to it the form of liquid water, and which had been perfectly insensible, or latent, until the formation of ice commenced. If the water had taken ten minutes to cool from 52° to 32°, it will be found to require one hour and ten minutes to become completely frozen; and hence, as in the same time it loses the same quantity of heat, the external air remaining equally cold, the latent heat is $20° \times 7 = 140°$, as in the former experiment. Another mode of verifying the result consists in exposing a pound of ice at 32°, and a pound of water at the same temperature, to the same source of heat, as on a steady fire, and it will be found that, by the time the ice has completely melted, the temperature of the water will have risen to 172°.

Water is, of all liquids, that which contains the greatest quantity of latent heat, and hence that which changes from the liquid to the solid state most slowly; and inversely, ice is the solid which absorbs most heat, and requires most time to liquefy. This property of water is of the highest importance in the economy of nature, for by means of it the change of seasons is rendered much less sudden than could otherwise occur. If water passed from 32° to 31°, and became solid by losing only the same quantity of heat as it gives out in cooling from 33° to 32°, the change of seasons would be so rapid and so uncertain as to interrupt almost entirely the proper cultivation of the soil, and, by the vicissitudes of heat and cold, become injurious to the health. But, as these properties of water are now arranged, each particle, in freezing, becomes a source of warmth to all around, and mitigates the severity of the cold; there can be but a comparatively small quantity of water rendered solid; and when, on the return of a warmer season, a sudden liquefaction might prove equally injurious, ice and snow, in melting, absorb all excess of heat, and render the change gradual, and suitable to the functions of those plants and animals to which a sudden transition might prove fatal.

We do not know the latent heat of many liquid bodies, but those given in the following table will suffice to show the remarkable

pre-eminence of water in that respect. The numbers are given in two columns; the first showing the interval through which the body itself, in its liquid form, would be heated by the heat it absorbs in melting, and the second showing the interval through which that heat would elevate the temperature of an equal weight of water Thus:

Latent Heat of	Measured by itself.	Measured by Water
Water	140	140
Sulphur	144	27·14
Lead	370	11·0
Zinc	493	48·3
Bismuth	550	23·25

In every case a solid body begins to melt at the same temperature Thus, ice never begins to melt until it arrives at 32°, and can never be raised above 32° without melting; consequently, the fixed point is the melting point of ice, and not the freezing point of water; for, if water be cooled carefully without agitation, its temperature may be lowered easily to 25°, and has been reduced to 15° without solidifying. This is a phenomenon like that which has been (page 25) noticed in the crystallization of sulphate of soda, where the solution may remain perfectly liquid until agitated, and then suddenly crystallizes with the evolution of considerable heat. If water, so cooled below 32°, be agitated, it freezes suddenly, and the temperature rises to 32°; the latent heat of that portion which freezes becoming sensible, and thus warming the entire mass.

Substances which crystallize easily generally expand in solidifying, and in doing so exert great force. Thus water is capable of bursting the strongest vessels if they be filled completely with it, and tightly closed so as to prevent expansion otherwise. It is by the agency of this force that the gradual deterioration of the surface of rocks, and the formation of the soil on the lower grounds, depends; the rain-water being absorbed into the pores and small cavities which even the hardest rocks contain, and being there, in winter, frozen, breaks open the substance of the rock, and causes it gradually to fall to powder, thus generating the soft and porous soil fitted for the reception and sustenance of the seeds and roots of plants. It is also by the action of this force of expansion, exerted by many bodies when they crystallize, that we are enabled to take accurate copies of the moulds into which such substances, in the liquid state, are poured. Cast iron, antimony, and the alloy of antimony used for printers' types, the alloy used for stereotype plates, brass, bronze, and all such bodies, are capable of making good castings by virtue of this expanding power; while bodies which do not distinctly crystallize, as gold, silver, and copper, are not capable of giving accurate castings, and hence the coinage of these metals is made by stamping the necessary marks upon them by means of a violent blow.

By the addition of small quantities of salts or vegetable acids, the freezing point of water may be considerably lowered: thus, sea-water does not easily freeze. When such a solution is brought to solidify, it is pure ice which first crystallizes out. Thus, from a strong solution of potash, ice has been obtained in large six-sided prisms; and the ice mountains which form in the Polar Seas are

found to be almost completely fresh. This principle has been applied also to the concentration of vinegar and lemon-juice by freezing, a large quantity of mere ice being formed round the sides of the vessel, and a central cavity remaining filled with concentrated acid.

The principle of latent heat has been applied to the production of artificial cold. For if a solid body suddenly liquefies without the application of external heat, it must abstract from the surrounding bodies the heat necessary to its liquefaction, and thus reduce their temperature and its own. Hence, when salts are dissolved in water without any chemical combination, there is cold produced. Thus, by mixing nitrate of ammonia with an equal weight of water, the thermometer sinks 46°; and carbonate and sulphate of soda, dissolved in three times their weight of water, reduce the temperature, the first 16°, and the second 12°.

In many cases where, by double decomposition, those soluble substances may be formed, more powerful effects are produced by mixing two salts together than by either separately. Thus neither nitre nor sal ammoniac produce much cold, but when mixed they generate nitrate of ammonia, which is very powerful, and hence cause a reduction of 40°. In other cases the cold results from a quantity of water of crystallization being set free and suddenly liquefying. Thus, when crystallized sulphate of soda is dissolved in muriatic acid, there are formed bisulphate of soda and chloride of sodium, with which but $\frac{1}{5}$ of the quantity of water remains; and the remaining $\frac{4}{5}$ being disengaged, and abstracting from the surrounding bodies the heat necessary for their liquefaction, depress the temperature through 50°.

By using snow or pounded ice, freezing mixtures of still greater power may be produced. The cold is the greatest when a substance is employed which contains itself a large quantity of water in a combined from. Thus crystallized chloride of calcium contains half its weight of water, and, when mixed with an equal weight of snow, the whole becomes liquid, and the quantity of heat absorbed is proportionally large. By combining such freezing mixtures intense degrees of cold have been produced; Mr. Walker, to whom the invention of most of them is due, having obtained a depression of temperature to —91° of Fahrenheit.

The following table contains the proportions for some of the most useful freezing mixtures, and the degree of cold which can be obtained by means of them. It is to be remarked, that in using freezing mixtures a great deal of the success depends on the rapidity with which the liquefaction is produced; the thinnest possible vessels, and a tolerably large quantity of materials should be used. For producing a great degree of cold, it is also necessary to cool the materials previously as much as possible; thus, to produce the intense cold of —91°, Mr. Walker had cooled the substances to be mixed dowr to —68° by means of other freezing mixtures.

FRIGORIFIC MIXTURES WITHOUT ICE.

Mixtures.	Parts.	Thermometer sinks	Degree of cold.
Nitrate of ammonia . . Water	1 1	from +50° to +4°	46°
Muriate of ammonia . . Nitrate of potash . . . Water	5 5 16	from +50° to +10°	40°
Sulphate of soda . . . Diluted nitric acid . . .	3 2	from +50° to —3°	53°
Sulphate of soda . . . Muriate of ammonia . . Nitrate of potash . . . Diluted nitric acid . . .	6 4 2 4	from +50° to —10°	60°
Sulphate of soda . . . Nitrate of ammonia . . Diluted nitric acid . . .	6 5 4	from 50° to —14°	64°
Sulphate of soda . . . Muriatic acid	8 5	from +50° to 0°	50°
Phosphate of soda . . . Nitrate of ammonia . . Diluted nitric acid . . .	5 3 4	from 0° to —34°	34°

FRIGORIFIC MIXTURES WITH ICE.

Mixtures.	Parts.		Thermometer sinks	Degree of cold.
Snow or pounded ice . . Common salt	2 1	from any temperature	to —5°	*
Snow or pounded ice . . Common salt . . . . Sal ammoniac	5 2 1	from any temperature	to —12°	*
Snow or pounded ice . . Common salt . . . . Sal ammoniac . . . . Nitrate of potash . . .	24 10 5 5	from any temperature	to —18°	*
Snow or pounded ice . . Common salt . . . . Nitrate of ammonia . .	12 5 5	from any temperature	to —25°	*
Snow . . . . Diluted nitric acid . . .	7 4		from +32° to —30°	60°
Snow . . . . Crys. muriate of lime .	2 3		from +32° to —50°	82°
Snow . . . . Potash	3 4		from +32° to —51°	83°
Snow . . . . Diluted nitric acid . . .	3 2		from 0° to —46°	46°
Snow . . . . Crys. muriate of lime .	1 2		from 0° to —66°	66°
Snow . . . . Diluted sulphuric acid .	8 10		from —66° to —91°	25°

In the ordinary experiment of freezing mercury by a mixture of snow and crystallized chloride of calcium, success is seldom obtained unless by having two portions of the mixture, and either cooling the materials for the second by means of the first, or plunging the tube of mercury, when it has exhausted the cooling powers of the first, into the second and freshly-mixed portion of materials.

There are many cases in which heat is evolved from solid bodies without our being able positively to ascertain its source, and where,

consequently, it may be considered as having previously been latent Thus, by the friction of two different bodies together, as when the axle of a carriage becomes hot, or when, as among savage nations, fire is obtained by rubbing two pieces of wood together. But it is rather a misuse of words to say that the heat evolved had previously been latent, for the latent heat of a body should properly be considered as that by which the fluid condition is conferred upon it, and hence a solid body cannot be said to have such latent heat at all. It is most likely that, as a diminution of specific heat accompanies the increase of density which occurs when oil of vitriol and water are mixed together, so where, by compression, the density of a solid body is increased, its specific heat may be diminished, and hence sensible heat evolved. Although our knowledge of this subject is not at all as satisfactory as its importance merits, it has been ascertained that, when iron is violently compressed, as in boring cannon or by repeated hammering, its specific heat becomes much less, and the heat evolved is so considerable that the metal may easily be made red hot. It would be well to distinguish between heat, certainly before latent, which may thus be rendered sensible, and the true latent heat which is absorbed during liquefaction, and which can be only given out again by the reassumption of the solid form; and this might be done, perhaps, and its connexion with specific heat made evident, by adopting the word *special heat*, or heat peculiar to the body. Thus liquids and vapours only can contain latent heat; but every body contains a quantity of *special heat*, equally insensible to the thermometer, but becoming manifest when the specific heat is diminished. The special heat is thus the heat which gives to the body the temperature which it possesses, and the quantity of special heat necessary to produce a rise of temperature measures the specific heat.

Many bodies undergo, before liquefaction, remarkable changes in their molecular constitution: thus iron, wax, and glass become soft and pasty, so that different pieces may be perfectly united into one; and it is, indeed, on this property that the most useful applications of glass and iron in ordinary life depend. This has been referred to a certain quantity of latent heat having already entered into the body, and giving an intermediate condition, that of semifluidity. There is no proof either for or against this view, as no exact experiments have been made upon such bodies. In other cases, where semifluidity is produced, as in lard, tallow, &c., it is plainly seen to arise from the substance being a mixture of two bodies, of which one melts easily, and, being then liquid, forms with the other, which remains still solid, a kind of pulp, which gradually becomes less thick, according as the temperature rises, until all is liquefied

SECTION IV.

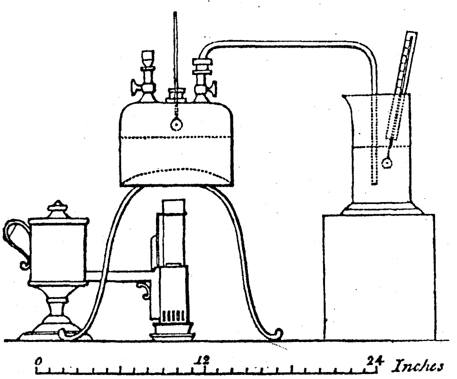
OF VAPORIZATION.

By the application of a higher temperature than that which was necessary for liquefaction, the generality of fusible bodies are capable of being converted into vapour. In this form they resemble, in molecular constitution, the most permanent of the gases, and are subjected

to precisely the same laws of change of volume, for any alteration of temperature or pressure, as atmospheric air, as long as the elastic form is preserved. This passage from the solid or liquid to the gaseous state of aggregation, may occur either slowly and silently, or with violence and rapidity; the body may either evaporate or boil. The evaporation may go on at any temperature, even at the lowest; but boiling commences only at a certain temperature, which depends on the nature of the body, and upon the pressure to which it is subjected. Each of these modes of generating vapour will require to be specially examined; but it is necessary to attend, in the first place, to the phenomenon which accompanies and may be supposed to produce the change of form, the absorption of the heat of vaporization; for precisely as a solid absorbs heat in becoming liquid, so does a liquid, in assuming the vaporous condition, render heat latent, and even in still greater quantity.

If we place upon a steady fire or over a lamp a cup of water, we shall observe that its temperature rises until it begins to boil, but then remains perfectly stationary until the last drop of the water shall have been boiled away. If we remark the time, we shall find it to be in the following proportion. Let us suppose the temperature of the water to have been originally 62°, and that at the end of six minutes it began to boil, having attained the temperature of 212°. In each minute, therefore, there entered into the water a quantity of heat sufficient to raise its temperature $\frac{212-62}{6}=25°$. Now, the source of heat remaining perfectly steady, it will be found necessary to apply it during 40 minutes to boil away all the water; and as in each minute there enters heat enough to raise the temperature of the same weight of water 25°, the total quantity of heat absorbed by the water in being converted into steam would have raised its temperature, had it remained liquid, $25\times40=1000°$, or just to redness. And yet this becomes perfectly latent, the temperature of the vapour formed, that is, of the steam, being exactly 212°, that of the water it is formed from.

By the inverse process a corresponding observation may be made. Thus, water being boiled in a vessel, as in the figure, the steam may be conducted by a tube into a glass containing a weighed quantity of cold water, the temperature of which is accurately marked. The steam, by condensing in the cold water, raises its temperature; and when a sufficient rise has been produced, the steam may be shut off, and the glass with the warm water weighed again. It is found to be heavier than before, from the quantity of water added to it by the condensation of the steam; and the quantity of heat given out by the steam in so condensing may easily be calculated. Thus: let us suppose that there were eight ounces of water, at 60°, originally used, and that, at the termination of the experiment, there were nine ounces at the temperature of 188°. It is then evident that one ounce of steam, in conden-



sing, had raised the temperature of the eight ounces 128°. The temperature of one ounce might have been, therefore, raised $128 \times 8 = 1024°$: but this was not all latent heat; for the steam, by merely condensing, should have formed liquid water at 212°, whereas it cooled to 188°. The difference, $=24°$, must be subtracted from the 1024°; and thus the latent heat of steam determined to be 1000°, as it had been found by the previous process.

The great quantity of heat thus contained in an insensible form in steam is very generally made use of for warming apartments and for chemical operations, in which exposure to the direct action of a fire, or even to a sand bath, might be injurious. By means of a series of pipes, steam from a boiler, placed at a distance, is brought to circulate through every part of the most extensive buildings, and condensing gradually as it passes along the cooling surfaces, the liquid water is conducted back again to the boiler, there to be reconverted into steam. In large manufacturing laboratories, such as those of the Apothecaries' Halls of Dublin and of London, there are steam ranges, or series of evaporating pans and stills, set in cast-iron cases, within which steam is introduced, and thus the most delicate vegetable preparations, such as extracts and inspissated juices, prepared at temperatures which, being completely under the control of the operator, allows all the freshness and active properties of the plants to be perfectly preserved.

By means of apparatus similar in principle to that in the last figure, the latent heats of the vapours of many fluids have been determined. It has been found that the latent heat of equal weights of the vapours of the following bodies would have raised the temperature of an equal weight of water in condensing:

Water	1000°
Alcohol	376°
Ether	163°
Oil of turpentine	138°
Nitric acid	335°

The latent heats of bodies, such as vinegar and water of ammonia, which have no definite chemical constitution, but contain mixed water, do not possess any value or importance.

In changing from the liquid to the gaseous state, the volume is increased in a very great degree; the amount of increase, in some instances, which may be taken as examples, is given in the following table.

Substance.	Spe. Gra. Water = 1000.	Boiling Point.	Volume of Vapour at boiling Point.	Volume of Vapour at 212°.	Specific Gravity of Vapour.
Water	1000	212°	1696	1696	620
Alchol	907	172°	488	519	1601
Ether	715	97°	240	289	2583
Oil of turpentine	867	315°	221	192	4763
Mercury	13500	660°	3395	1938	6969

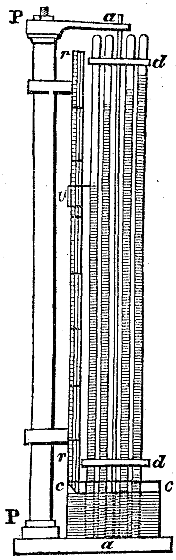
In the first column are the names of the bodies; in the second, their specific gravities, water being 1000; in the third, their boiling points; in the fourth, the number of volumes of vapour furnished by one volume of each fluid at its boiling point; in the fifth, the number of volumes of vapour reduced to a standard temperature, 212°, which one volume of fluid may produce; and in the sixth, the specific gravity of the vapour, air being 1000.

It has been imagined that there should exist some physical connexion between the increase of volume produced by the change from the liquid to the gaseous state, and the quantity of heat rendered latent during the change; and it is, in fact, generally true, that those bodies which have small latent heat expand least, as oil of turpentine and ether. But, as yet, from the few experiments that have been

made upon latent heats, with substances sufficiently pure to be taken as the basis of calculation, nothing positive can be considered to be known.

The passage from the liquid condition to the state of vapour is distinguished from the change of a solid to a fluid, by the important fact that, while liquefaction is definitely produced at one temperature, and at that alone, vaporization occurs at all temperatures; and it is only from the influence of external circumstances that the change is accompanied, at a particular temperature, by the phenomenon of boiling. The coldest water is capable of forming vapour; even ice evaporates; and, in order to do so, it is not necessary that it shall previously melt; it is thus that snow will gradually disappear from the ground, even when shaded from the sun's rays, and though the air shall have continued below the melting point. Other solid bodies also evaporate without previous melting, as camphor; and arsenic cannot be melted; for, when heated, it is converted at once from the solid to the vaporous condition. The particles of volatile bodies appear thus, at all temperatures, to repel each other to a certain degree, and to spread abroad, in the form of vapour, until they occupy completely the space in which the body is contained, and exercise a pressure which is equal to the force of their mutual repulsion, and which is termed the elasticity of the vapour.

The amount of elasticity, or, as it is often called, tension of a vapour, is determined by very simple methods. Thus, for elasticities



below that of atmospheric air, a series of barometer tubes arranged in a stand, P P *a a*, are to be carefully filled and inverted in a basin of mercury, *c c*, as in the figure. One such tube, *d d*, is to be kept untouched, to measure the elasticity of the external air. If a little water be allowed to pass up into the next tube, and there float upon the surface of the mercury, it immediately forms vapour, which spreads through all the empty space, and, pressing against the upper surface of the mercurial column, counteracts a portion of the pressure of the external air. The remaining pressure of the air is able to support, therefore, only a shorter column of mercury, and the height of the mercury in the tube diminishes. If into another tube some alcohol be introduced, there is a similar, but still greater depression of the mercurial column caused, and with ether the height of the mercurial column is still more diminished. The atmospheric pressure in these cases balances the shortened column of mercury added to the elasticity of the vapour, and this last is consequently measured by the height of the column of mercury which it is capable of replacing, that is, by the space through which the mercury has been depressed, which is read off by the rule and index, *r v r*. Thus, if the barometer be at 30 inches and the temperature 80°, the mercury will stand in the tube with watery vapour at 29 inches, in that with alcohol at 28·1, and in that of ether at 10 inches. The elasticities of these vapours are therefore at the temperature of 80°.

Vapour of water	1·0 inch.
" of alcohol	1·9
" of ether	20·0

In order to ascertain how the elasticity of a vapour changes with the temperature, it is only necessary to enclose the upper part of the tube in a cylindrical case containing water or oil heated to the necessary degree. As the heat increases the height of the mercurial column will diminish, and at each temperature the elasticity is so determined. The apparatus may be modified by bending the tube so as to immerse the bent portion containing the vapour into a globe of water or oil to which heat may be applied, but the principle remains the same. In this way a table of the elasticity of a vapour at all temperatures below their boiling points may be formed; and as there will be frequent reference hereafter to the tension of the vapour of water, the following table is introduced for use and as an example:

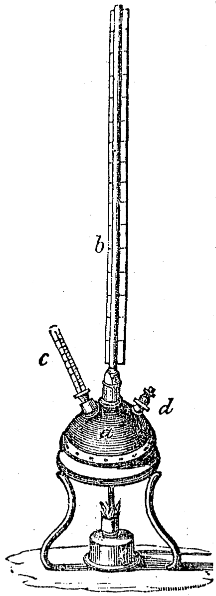
Temperature.	Elasticity. (in inches of mercury.)	Temperature.	Elasticity. (in inches of mercury.)
32°	0·200	90°	1·36
40°	0·263	100°	1·86
50°	0·375	120°	3·33
55°	0·443	140°	5·74
60°	0·524	160°	9·46
65°	0·616	180°	15·15
70°	0·721	200°	23·64
80°	1·000	212°	30·00

When a liquid, in such an apparatus, is heated until the vapour formed occupies all the tube and expels the mercury, the elasticity of the vapour is equal to that of the air, and the liquid exposed to the air boils; the phenomenon of boiling arising simply from the fact that the elasticity of the vapour balances the pressure of the air while the bubble is passing through the fluid: thus, suppose a vessel of water exposed to the air at 200°, and a bubble of steam to form in it; the pressure exercised by that bubble being equal to its tension, is equivalent to a column of 23·64 inches of mercury; but the external pressure being 30 inches, the bubble is crushed in by a force equal to the difference (6·36 inches of mercury), and, consequently, dispersed. If the water, however, be heated to 212°, the elasticity becomes equal to 30 inches, and then the external and internal pressures being equal, the bubble rises in the liquid without injury, and maintains itself at the surface until its investing film of water is ruptured by other causes, when the vapour mixes uniformly with the air.

It is the bursting of the steam bubbles that are first formed in this manner that constitutes the simmering of a boiler or the singing of a kettle on the fire. The bottom of the vessel heats more strongly the layer of water in contact with it, so that the steam has there a high degree of elasticity, and forms a multitude of minute bubbles; when these separate from the hot metal, they are immediately burst in by the greater external pressure, and the mass of water is thus thrown into a state of exceedingly rapid and uniform vibration, which fall upon the ear so regularly, in many cases, as to produce a musical and often agreeable tone, which may become

graver or more acute, according as the bubbles burst more or less rapidly after one another.

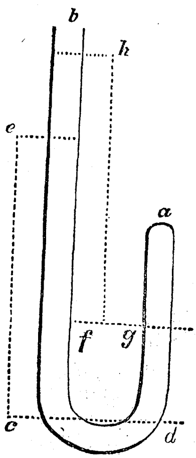
The elasticity increases very rapidly with the temperature, as is seen in the table, where, in rising from 180° to 212°, the elasticity is doubled. For high temperatures the rate of increase is still more rapid. To determine the elasticity at temperatures above the ordinary boiling point, an apparatus completely cut off from the external air is made use of. In the figure there is a globular vessel of strong metal, *a*, into which is introduced by the stopcock *d*, the fluid to be experimented on, as, for example, water. In the aperture *c* is fitted a thermometer, the bulb of which dips into the fluid near the centre, and shows its temperature. A quantity of mercury being in the bottom of the vessel, the tube *b* dips under its surface, and, rising to the necessary height, has attached to it the scale divided into inches and their parts. When the apparatus is heated, as the vapour produced cannot escape, all junctures being perfectly steam-tight, the temperature rises continuously in place of stopping at the boiling point, and the vapour formed pressing on the surface of the remaining liquid, and by it on the mercury underneath, forces the mercury up the tube *b* until the mercurial column shall have attained such a height as to counterbalance by its weight the elasticity of the vapour. In these cases the elasticity is generally reckoned by atmospheres, each atmosphere being equivalent to a mercurial column thirty inches high. In this manner the vapour of water has been found to exert a pressure of



1 atmosphere at	212°	16 atmospheres at	398°
2 atmospheres at	250°	20 " "	418°
3 " "	275°	25 " "	439°
4 " "	294°	30 " "	457°
6 " "	320°	40 " "	486°
8 " "	342°	50 " "	510°
12 " "	374°		

It is necessary, in order to understand such tables, to observe that this great increase of the elasticity of steam, as the temperature rises, results not from the expansion of steam already formed, but from the constant addition of new quantities of steam for every variation of temperature. If a globe full of steam at 212°, but containing no liquid water, were heated to 294°, it would tend to expand precisely as air or any other gas, and the increase of elasticity would be only from 30 to 34 inches, or from 1 atmosphere to $1\frac{1}{8}$; but if the globe contain liquid water, there is such an additional quantity of vapour formed and compressed into the same space, that the elasticity becomes equal to four atmospheres, or to 120 inches of the mercurial column. Also, when the pressure on vapour is made to vary, the result deviates from the rule laid down

in page 20, for the action of pressure upon gases; for the elasticity of a vapour cannot be really increased by any increase of pressure: it remains the same, but a quantity of the vapour becomes liquid, and there continues in the state of vapour only as much as occupies with the same elasticity the diminished volume which the column of mercury leaves. Thus, if we consider the bent tube *a b*, of which the extremity at *a* is closed, and the leg *a* occupied from the dotted line *c d* by vapour of ether at its boiling point, and balancing in the leg *b* a column of mercury thirty inches high. If, now, without allowing the temperature to change, mercury be poured in at the orifice of *b* until it shall rise in *a* up to the line *f g*, and occupy exactly one half of that leg, the vapour will not be compressed into half its volume, and, acquiring a double elasticity, support 60 inches of mercury as a gas should do, but one half of the ether will assume the liquid form, and the remainder, occupying the remaining half of the original volume, will balance 30 inches of mercury precisely as it did before, and the pressing column, counting from the line *f g*, will terminate at *h*.



If, however, in place of attempting to increase the pressure on a vapour, we diminish it, then the vapour preserves its elastic form, and its elasticity diminishes in all respects as if it were a gas.

The specific gravity of a vapour, formed at any certain temperature, should be proportioned simply to the elasticity, if the volume were not altered by the change of temperature, and it should be inversely as the volume if it could all remain uncondensed; but, in reality, the relation is more complex, and may be calculated upon the following principles. Thus, if we wish to know the specific gravity of vapour of water having an elasticity expressed by 7·42 inches of mercury, and the temperature 150°, we proceed as follows: the specific gravity of steam at 30 inches and 212° is 620·2; and hence, if the volume did not change, the specific gravity of the vapour at 150° should be $620{\cdot}2 \times \frac{7{\cdot}42}{30{\cdot}00} = 153{\cdot}39$; but in cooling from 212° to 150°, the portion of steam which retains its elastic form is compressed within a smaller volume, and hence has its specific gravity increased in proportion to the change, and therefore the 153·39 obtained above must be increased in the proportion of the volume at 150° to the volume at 212°, or as 611 : 673, and thus becomes 169·24. The subjoined table contains specific gravities for some temperatures calculated in that way, and accompanied by the temperatures, the elasticities, and the weight in grains of 100 cubic inches of the vapour.

Temperature.	Elasticity in Inches of Mercury.	Specific Gravity. Air=1000.	Weight of 100 cubic Inches.
32°	0·200	5·68	0·1361
50°	0·375	10·17	0·2474
60°	0·524	14·06	0·3387
100°	1·860	46·36	1·1028
150°	7·420	169·24	4·0543
212°	30·000	620·20	14·9600

There is some reason to suspect, however, that vapours do not follow exactly the theoretic rules upon which such tables are constructed, and which, in reality, apply only to gaseous bodies. Thus, Despretz has found the specific gravity of the vapour of water to be at 67° 7·72, while by this calculation it should be 17·26, air at 212° being 1000; his results cannot be considered as decisive, although they show the necessity for an accurate re-examination of the subject. At very high tempera-

tures, the elasticity does certainly not increase with the specific gravity when the volume remains constant. Ether is found to become gaseous, and to occupy only twice the volume it had when liquid, at the temperature of 320°, and its elasticity in that state equals 38 atmospheres, whereas, by calculation, its elastic force should be 168 atmospheres. Alcohol, enclosed in tubes hermetically sealed, is totally converted into vapour, occupying only three times the volume of the liquid at 404°, and then exerts a pressure only of 129 atmospheres, while by theory the pressure should equal 221. Water, also, was obtained by Cagniard de la Tour gaseous in four times its liquid volume at 773°, and should then, by theory, have an elasticity of 780 atmospheres, a force far above what the glass tube employed could possibly have resisted. It would appear, therefore, that vapours, so far as the relation between their specific gravity and their elasticity is concerned, do not follow exactly the same law as gases except within certain limits; but that, when the elasticity is much smaller or much greater than the atmospheric pressure, variations which are very remarkable, though not as yet well understood, present themselves.

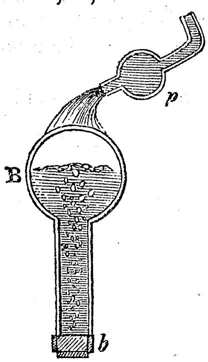
When a vapour, as, for example, steam, which has been generated in close vessels, and attained a great elasticity, is suddenly allowed to escape into the air, its temperature is suddenly reduced in a remarkable degree, even independent of condensation. If the steam had been formed under a pressure of four atmospheres, its volume is but one fourth of what it should become when free, and hence, on escaping, it expands in that proportion; under that pressure its temperature had been 294°, but by the increase of latent heat it falls immediately to 212°; there, however, the expansion does not stop; the impulse of the particles of vapour carries them much farther; and as the specific heat increases so as nearly to be doubled when the volume becomes doubled, a considerable reduction of the temperature below 212° occurs, which is still farther increased by admixture of cold air which presses into the rarefied space left by the expansion of the steam. Hence it is that steam escaping into the air from under considerable pressure possesses much less heating power than steam arising from water boiling in an open vessel: it is much less liable to scald.

The principle of the conversion of a solid or liquid body into a vapour at all ordinary temperatures is true, even where the body may be very little volatile. Thus the space over the mercury in the best barometers is not truly empty, but contains a quantity of mercurial vapour, exercising a certain elasticity, and, by depressing the liquid column, making the pressure of the external air appear smaller than it really is. It would appear, however, that there are, for some bodies at least, temperatures below which evaporation does not go on; thus no mercurial vapour can be detected unless the temperature be above 40°, and oil of vitriol requires to be heated to 120° before any vapour forms from it: it is probable, however, that even in these cases the general principle holds good, and that it is only from the minute quantity of vapour eluding our means of research that the existence of a limit to evaporation was believed.

The boiling point of a liquid being that at which its vapour can support the external pressure, it is liable to constant fluctuation as the pressure changes, and hence the fixing of the temperature of boiling water upon the thermometer requires the care and attention already noticed. If the barometer stood at 23·64, water would boil at 200° in place of 212°; and so close is the connexion between the pressure and boiling point, that the height of any place above the level of the sea may be determined by the temperature at which

water boils there. Thus, if, on heating some water on the summit of a mountain, it be found to boil at 203°, we find, by reference to a table, that the elasticity of its vapour is then 25·1 inches, and hence that in the same place, at the same moment, the column of mercury in a barometer should have been at that height. Then, by the ordinary calculation, the height of the mountain may be found with as much accuracy as if the barometer itself had been carried up. On the summit of Mount Blanc, the highest point of Europe, water has been found to boil at 184°.

By reducing, artificially, the amount of pressure upon a fluid, as by placing the vessel containing it under the receiver of an air-pump and exhausting the air, the boiling point is lowered in a remarkable degree. If the vacuum were perfect, a fluid would boil even at the lowest possible temperature; but this is not practicable, as the vapour formed cannot be so perfectly removed but that it will exercise some pressure; but, with a good air-pump, fluids may be got to boil 145° below their ordinary boiling points; thus water will boil at 67°, alcohol at 32°, ether at a temperature at which quicksilver would freeze. If, at the moment that such a fluid is in violent ebullition, the working of the pump be stopped, the vapour accumulates, and, exercising on the surface of the fluid an amount of pressure corresponding to its elasticity at the existing temperature, raises the boiling point, and thus stops the ebullition. This fact may be shown in a very simple and singular manner, by half filling a flask, B, with water, and boiling the water until all the air in the flask shall have been expelled, and then carefully closing the mouth of the flask, *b*, by an airtight cork. On removing the source of heat, the upper part of the flask, B, when inverted as in the figure, remains full of vapour, which, pressing upon the liquid water, arrests the ebullition. If, then, a jet of cold water, *p*, be allowed to play upon the flask, the vapour is condensed, and, a vacuum being thus produced, the water begins to boil; if a jet of warm water be employed, the vapour retains its elastic form, and the ebullition ceases, so that in this apparatus the application of cold may appear to cause, and that of heat to prevent, the water's boiling.



The temperature at which a liquid boils is thus totally dependant on the amount of pressure to which it is subjected. But the limits within which that pressure varies near the level of the sea, in ordinary cases, are so small, that the boiling point may be looked upon as one of the most important characteristic properties of a volatile substance; and from the facility with which it may be determined, it is almost universally capable of being applied. Hence, in describing such bodies, the boiling point will be in all cases given; but, for illustrating the present subject, a table of the boiling points of some of the most remarkable liquids is subjoined:

Muriatic ether	52°	Water	212°
Sulphuric ether	96°	Nitric acid	248°
Sulphuret of carbon	116°	Oil of turpentine	315°
Pyroacetic spirit	132°	Phosphorus	554°
Water of ammonia	140°	Sulphur	601°
Pyroxylic spirit	151°	Sulphuric acid	630°
Alcohol	173°	Mercury	660°

The boiling point is influenced by some other circumstances than the atmospheric pressure; the nature of the vessel may alter it several degrees. Thus, in a glass or glazed porcelain vessel, water boils, under a pressure of 30 inches, not at 212°, but 214°; and in graduating a thermometer, it is hence necessary to use a metallic vessel. This latter appears to favour ebullition by the minute irregularities on its surface, affording a nucleus for the steam to form, as a crystal dropped into a saline solution facilitates the crystallization; and if the smooth surface in the glass vessel be removed in a single point by a scratch with a diamond, the bubbles of steam will be seen to form there before the general mass of liquid comes to boil. The influence of roughened or angular surfaces in thus favouring the escape of steam, may be shown very well by heating water in a glass flask to boiling, and then allowing it to cool a little, so that the boiling shall completely cease; if, then, a little filings of copper, or a platina wire, be dipped into the liquid, if the cooling had not gone too far, the boiling will immediately recommence, the steam forming at the edges and angles of the rough substances introduced.

The temperature of the steam produced is not affected by the boiling point of the liquid. Thus, although by dissolving salts, such as chloride of calcium, in water, its boiling point may be raised to 264°, the temperature of the vapour immediately over the solution is found to be but 212°; for, though the temperature of a steam bubble which rises up through such a solution must be 264°, yet, as its elasticity and latent heat are proportional to that temperature, it expands on mixing with the less elastic atmospheric air, and is cooled down instantly to the ordinary boiling point. The heat of a water-bath may thus be increased by the addition of saline bodies; but the temperature of a steam-bath depends only on the elasticity of the steam.

A curious, though only apparent, anomaly in the relations of liquids to their boiling points consists in the possibility of the vessel containing the liquid being heated even to redness without the liquid boiling, though exposed only to the ordinary pressure. This may easily be shown by heating a platina crucible to redness, and dropping into it a small quantity of water; the water remains on the red-hot metal without disturbance, and appears scarcely to evaporate; but if another crucible be heated to 300°, and the water be poured out of the first into the second, it instantly boils, and is dissipated in a gush of vapour. The reason is, that in the red-hot crucible the water is not really in contact with the metal, and hence the heat passes to it with extreme slowness; but the water wets the colder crucible, and, absorbing from it all the necessary heat, is instantly converted into steam. The cohesive force of the metal to the water being diminished considerably, this lies in a red-hot crucible as a clean steel needle floats on water, or a globule of mercury moves

upon glass, and is not affected by the heat until it wets the vessel, just as the needle does not sink in the water until it is wetted by it. At certain temperatures all liquids manifest the same peculiarity.

When a liquid evaporates at a temperature below its boiling point, it still absorbs and renders latent a great quantity of heat, and, indeed, more heat than it would render latent when converted into vapour by ordinary boiling. It has been found, by accurate experiments with water, and there is good reason for supposing it to hold also with liquids in general, that no matter at what temperature a liquid vaporizes, it absorbs the same total quantity of heat. The more of this that becomes sensible, the less is the portion which remains latent, the sum of the latent and sensible heats of the vapour being at all temperatures the same. Thus, with water evaporating at

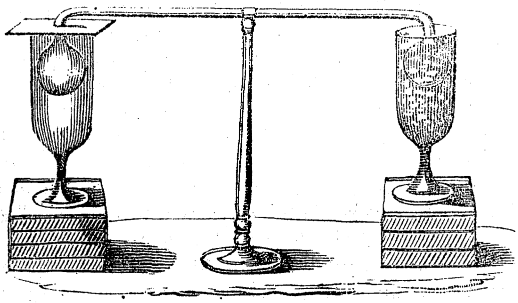
32°, the latent heat is			1180, the sum being			1212
100°,	"	"	1112,	"	"	1212
212°,	"	"	1000,	"	"	1212
300°,	"	"	912,	"	"	1212

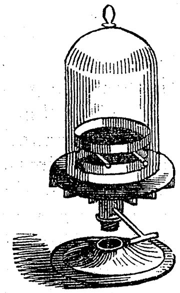
There is, therefore, no economy in evaporating or distilling at one temperature rather than another, as the same absolute quantity of heat is necessary for the formation of the steam; but, for other reasons, the formation of vapours at low temperatures affords to the chemist processes of the greatest value. Many vegetable substances undergo important alterations in their chemical constitution and medicinal properties if they be exposed for a long time even to a heat of 212°; and hence, in the preparation of extracts and inspissated juices of plants, in pharmacy, forms of apparatus are sometimes employed, in which the evaporation is carried on in close vessels connected with an air-pump, and in which a partial vacuum, measured by a barometer gauge, may be established. In the manufacture of sugar, this principle of evaporation at low temperatures, by removal of the atmospheric pressure, was the source of great improvement, as the true crystallizable sugar is converted into the uncrystallizable sugar (treacle) with great rapidity at the temperature of boiling sirup, and was hence, to a great extent, lost to the manufacturer. By later improvements in the mode of applying heat, the necessity of evaporating the sirup in vacuo has been, however, completely obviated.

The absorption of heat in the conversion of a liquid into a vapour, at ordinary temperatures, may become the source of considerable cold; and it is, indeed, in this way that the greatest cold yet generated has been produced. The cold which is felt when a little ether or spirits of wine is dropped on the hand, arises from this fact; and by surrounding the bulb of a mercurial thermometer with some loose cotton, and moistening it with liquid sulphurous acid, the quicksilver in the bulb may easily be frozen. By placing some ether in a shallow, thin metallic cup, which rests in a glass vessel containing a small quantity of water, and producing, by the air-pump, the rapid vaporization of the ether, the water may be so frozen that the two cups shall adhere firmly together by the intervening sheet of ice.

Water may be even frozen by its own evaporation, as in the cryophorus, which consists of a long tube terminating in bulbs which contain some water, and from which the air had been carefully ex-

pelled by boiling before the apparatus was completely closed. The space above the water remains then occupied only by watery vapour. If all the water be brought into one bulb, and the other bulb be immersed in a freezing mixture, the vapour will condense there, and new vapour being formed, a distillation will be produced from the one to the other bulb. The vapour which forms in the warm bulb must derive its latent heat from the water which remains behind, and this is gradually cooled to the freezing point, and ultimately completely frozen; the latent heat of about eight parts of water being given up to form the latent heat of one part of vapour at 32°. Even without the application of artificial cold, water may be frozen by its own evaporation. Thus, if under the receiver of an air-pump we arrange two flat dishes, the upper containing water, the lower containing oil of vitriol, and then, having removed the air, we leave the apparatus for a short time to act, we shall find the water in the upper vessel converted into ice. Accordingly, as any portion of vapour forms, it is immediately absorbed by the sulphuric acid, which has a great affinity for water; and the vapour being thus prevented from collecting, the loss of heat by evaporation proceeds unceasingly, until so much heat has been removed that the residual water is converted into ice.





In fluids more volatile than water, this synchronous freezing and evaporation may occur still more simply. Thus, if strong prussic acid be allowed to form a pendant drop from a glass rod, the drop will become solid by the evaporation of one portion of it, and the cooling of what remains. The remarkable phenomenon of the solidification of carbonic acid arises from the same principle. A jet of liquid carbonic acid being allowed to escape into the air, one portion instantly flashes into the state of gas, and absorbs so much heat that the portion which remains is converted into a compact solid mass.

In warm climates, the evaporation of water is commonly employed to moderate the sultriness of the air, by the agreeable cold and freshness it produces. The Spanish *alcarrazas* are earthen vessels, so porous that any liquid which is put in them gradually filters through, and, evaporating from the outer surface, cools the interior mass. In chemical operations, the same mode of refrigeration is in constant use; and when describing these operations, the action of this principle, in the construction of the apparatus used, will be referred to.

The conversion of a liquid into vapour at ordinary temperatures

is often called spontaneous evaporation; and in the case of water, from the great extent to which it becomes subservient to the economy of nature, this process is one of high importance. It was formerly supposed that the atmosphere was necessary to evaporation; and this idea was strengthened by the fact, that by a current of air the evaporation is much assisted; but it is now established that the pressure of air is really an obstacle to evaporation, and that a current is useful, not by supplying new quantities of air, but by removing the vapour according as it is formed, and leaving fresh spaces into which it may expand. When a liquid forms vapour, the quantity formed is determined only by the space into which the vapour may spread, and by the temperature. It is no matter whether the space be occupied before by other vapours or by air, or whether it be a vacuum; the quantity of vapour which can form in it is in all these cases the same.

Dalton was the first who clearly showed that different gases and vapours offer no resistance to each other's elasticity: thus, that the particles of watery vapour in the air are not subjected to the pressure of the atmosphere, but only influenced by the pressure of the particles of the same kind; and hence, that at 32°, when the elasticity of vapour is only 0·200 inch, it retains perfectly its elastic constitution, though diffused through an atmosphere, the elasticity of which may equal thirty inches. If we moisten the interior of a bell glass, filled by air, with ether, alcohol, sulphuret of carbon, and water, all mixed together, there will be formed in the bell as much of the vapour of each substance as if the bell had been completely empty of the others; each vapour will exercise a pressure proportional to its elasticity, and by the sum of all these pressures, the pressure of the external air will be equilibrated. It is, consequently, possible to produce the rapid evaporation of one fluid, while another beside it, or even mixed with it, shall not evaporate at all; it being only necessary to remove the vapour of the one as rapidly as it is formed, while the portion of the vapour of the second produced in the first instance shall remain, and prevent its farther change. Thus, by placing a shallow dish of dilute alcohol under the receiver of an air-pump, with a quantity of quicklime, the latter combines with and absorbs the watery vapour as fast as formed; and there is, hence, a continual evaporation of the water, while the alcohol, after generating as much vapour as once fills the receiver, is pressed upon by it, and cannot form any more. In this manner, alcohol, almost quite pure, though much the more volatile, in the ordinary sense, may be obtained by the evaporation of its solution in water, as it were to *dryness.*

If the liquid be in excess, the vapour possesses the elasticity belonging to its temperature; but if there be not liquid enough to form so much vapour, the vapour formed then expands, so as to occupy the entire space, and its elasticity diminishes in proportion to the increase of volume; vapours being regulated by the same law of pressure which holds with gases.

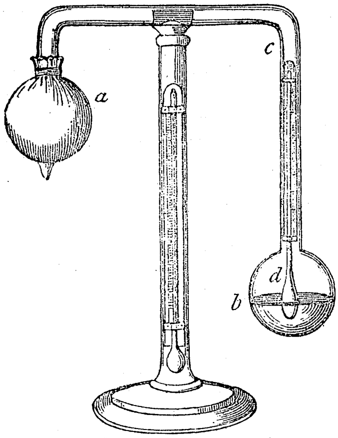
If, thus, a bell glass of atmospheric air be confined over water at the temperature of 80°, a quantity of vapour diffuses itself through the air, and, as there is water in excess, the elasticity of that vapour will be 1·00 inch. Now if we suppose the elasticity of the air to have been previously 30 inches, it will become, by the

addition of the vapour, 29, for the vapour counteracts one inch of the external atmospheric pressure; the air in the bell glass will then expand in the proportion of 30 to 29; or, what is the same in practice, the volume of the damp air is the same as the volume which the vapour should occupy, if condensed in the proportion of its own elasticity to the atmospheric pressure, added to the volume occupied by the air when dry. It is thus that the volumes of gases collected over water are corrected for the watery vapour that is mixed with them. Thus, in the analysis of a substance containing nitrogen, let us suppose that 8·54 cubic inches of nitrogen have been collected over water at the temperature of 63°, and the barometric pressure being 29·35 inches; at that temperature the elasticity of vapour is 0·58, and hence that of the dry air is 29·35—0·58=28·77. The volumes which they occupy are as these numbers, and hence the 8·54 of damp gas consists of $\frac{0\cdot58}{29\cdot34}\times8\cdot54=0\cdot17$ of watery vapour, and $\frac{28\cdot77}{29\cdot34}\times8\cdot54=8\cdot37$ of dry nitrogen.

This volume should still be corrected for temperature and pressure before the quantity of nitrogen by weight could be obtained from it.

Where the air is not completely saturated with the watery vapour, it is not so easy to determine the exact quantity of vapour which it contains. One of the best methods consists in cooling it until its volume is so much diminished that the quantity of vapour is sufficient to saturate it, and from the temperature at which this occurs the quantity of vapour may be calculated. This temperature is termed the dew point of the air or gas, because, if cooled in the least below that point, a quantity of liquid water is deposited in the form of dew upon the neighbouring cold bodies. This may be easily done by taking a tumbler of water somewhat too warm, and cooling it gradually by dissolving in it a little mixed nitre and sal ammoniac, until a slight deposition of dew is perceptible on the exterior of the glass; the water is then at the temperature of the dew point. Another method consists in observing the rapidity of evaporation from the surface of the bulb of a thermometer which is covered with muslin kept wet by water. The thermometer so arranged is always at a lower temperature than an ordinary thermometer, from the quantity of heat carried away by evaporation, and the temperature will be lower in proportion to the amount of evaporation. In dry air, evaporation is quickest; in air saturated with moisture evaporation ceases, and in all intermediate degrees there is a connexion between the quantity of moisture already present in the air and the depression of temperature, which accompanies the formation of as much more as will saturate it. This method is peculiarly of interest from the means which it afforded to Apjohn of ascertaining the specific heats of the gases already noticed, and it is easy now to understand the general principle upon which his process was established. If we consider a certain space which may be filled by the different gases in succession, and these gases being dry, they are made to saturate themselves with watery vapour, for the formation of which they themselves supply the heat, it will be easily seen, that as the quantity of heat to be given out is the same for all, their temperatures will be reduced in a degree inverse to their specific heats. Hydrogen with a high specific heat will only require to cool about one third the number of degrees necessary for air or other gases. The numerical results obtained by this process have been already given.

Instruments for the purpose of determining the quantity of the watery vapour which the atmosphere contains are termed hygrometers, and that of Daniell is one of the most elegant and most useful. It is a cryophorus, *a b c*, which in place of

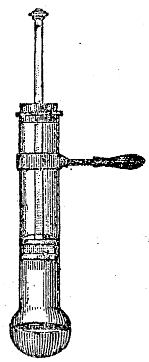


water contains ether, and in one bulb of which, *b d*, is fixed a very delicate thermometer. This bulb is made of blackened glass, and the other bulb, *a*, is covered with a little bag of muslin. All the ether having been made to pass into the black glass bulb, a little ether is poured on the muslin envelope of the other. This, by condensing the vapour inside, causes the ether to distil from the blackened bulb, and thus cools it and the air in contact with it, until it arrives at the point of saturation, when a dew of liquid water begins to be deposited, which is at once observed upon the blackened glass. The internal thermometer shows the temperature of the bulb, which is the dew point, and a thermometer which is attached to the support of the instrument shows the temperature of the external air.

When the dew point has been thus determined, the subsequent calculation is very simple. Thus, if there be air at 72°, of which the dew point is 45°, the barometric pressure being 30 inches, the elasticity of steam at 45° is 0·316 ; and as the elasticity diminishes according as the volume increases from 45° to 72°, the elasticity of the vapour in the air at 72° is 0·30 ; and the atmospheric pressure of 30 inches is produced by the dry atmosphere, which balances 29·70, and the watery vapour which balances 0·30 ; and the respective volumes are as these pressures.

Gay Lussac has sought to establish a close relation between the manner in which solid bodies dissolve in liquids, and that in which vapours diffuse themselves through space. Thus, if a solid body dissolved only because the liquid diminished the cohesion of its particles, the diminution of that cohesion in another way should increase the solubility very much: this, however, does not occur. When paraffine dissolves in alcohol, the solubility increases steadily with the temperature, and does not change more rapidly at the temperature when the paraffine melts than at any other. This is the case also with many other easily fusible bodies. Hence he compares the diffusion of particles of the solid through the liquid to the diffusion of particles of vapour of water through the air, which is not affected by the solid or liquid form of the water, but depends only on the temperature; and certainly this view, though not applicable to all, or even the majority of cases of solution, is of much interest, as pointing out a similarity between solution and vaporization previously unnoticed, and which may be applied to the explanation of many anomalous facts.

The employment of steam as a moving power is of so much importance to science and to the arts, that it would be improper to terminate a discussion of the properties of vapours without any allusion to the manner in which it is utilized. The little steam cylinder of Wollaston figured in the margin contains all that is essential to the application of steam, in principle, to produce motion. A glass tube, terminating below in a bulb, is fitted with a little steam-tight piston, which slides up and down, the rod passing through the brass cap at top. If, now, a little water be placed in the bulb and boiled, its steam, pressing on the bottom of the piston, forces it up; and when at top, if the bulb be dipped into cold water, the steam condenses, and the pressure of the external air forces the piston down again. This may be repeated any number of times, and is the essential element of the atmospheric steam engine of Newcomen. It was in this form when Watt commenced his improvements on it; and by applying all the resources of the exact knowledge of the properties of heat



then first obtained by himself and his illustrious associate Black, he converted it, though still without changing its fundamental principle, from the machine of Newcomen, which had been rejected from practice for its inefficiency and expense, into the instrument which, after the art of printing, must be considered as the most powerful material agent of human improvement and civilization of which mankind has ever obtained possession.

The similarity of constitution of gases and vapours has been already pointed out on many occasions, and particularly, in page 21, the conversion of gases into liquids by the application of great pressure has been detailed. A liquefied gas so contained in a close vessel is precisely in the condition of water heated in a digester, as in the apparatus figured in page 80, far above its boiling point, and generating steam possessed of considerable tension. On this analogy has been founded an interesting speculation concerning the temperatures at which the gases would, at ordinary pressures, assume their liquid form, that is, their boiling points when liquid, thus:

At 44·5° the tension of liquid nitrous oxide is	50 atmospheres.	
At 32·0° " " "	44 "	
For 12·5° an increase of tension of . . .	6 atmospheres.	
Steam exerts a pressure of 50 atmospheres at . . .	511·5°	
and of 44 " " . . .	497·5°	
For six atmospheres the difference is	14·0°,	or just the same.
Liquid carbonic acid exerts a pressure of 25 atmos. at	32°	Difference, 20°
and of 20 " "	12°	
The tension of steam is 25 atmospheres at	439·5°	Difference, 21°
20 " "	418·5°	
Muriatic acid exerts, when liquid, a tension of 25 atmos. at	25°	Difference, 22°
and of 20 " "	3°	
Steam balances 25 atmospheres at	439·5°	Difference, 21°
20 " "	418·5°	
Ammonia liquefies and exerts a pressure of 6·5 atmos. at	50°	Difference, 18°
and of 5 " "	32°	
Steam exerts a pressure of 6·5 atmospheres at . . .	326°	Difference, 18·5°
5·0 " " . . .	307·5°	

It is hence evident that, in every case, the rate of increase of elasticity of these gases with the temperature follows the same law as that of steam; and there is, therefore, good reason to believe that, if the elasticity were diminished to one atmosphere, the reduction of temperature necessary to effect it should be regulated by the same law as that of watery vapour; the gases should then, under the ordinary pressure of 30 inches, become liquid, and when liquid, their boiling points should be:

Nitrous oxide . . . . =	— 252·4°	Fahrenheit.
Carbonic acid . . . . =	— 230·8°	"
Muriatic acid . . . . =	— 202·0°	"
Ammonia . . . . =	— 63·4°	"

The great increase of elasticity which these liquefied gases acquire by a change of temperature, limited to a very few degrees, has led to sanguine opinions of their advantages as a source of power in machines. No experiments at all sufficiently satisfactory to be decisive upon the question have as yet been made.

There are some other properties of gases which, although closely connected with the subject now discussed, I shall postpone, in order to introduce them where they are found to be of the most practical importance. Thus, the manner in which gases spread through each other, in virtue of their diffusive power, will be descri bed under the head of Atmospheric Air, to the proper constitution of which this law is indispensable. The relation of gases to water, their solubility in that and other liquids, and the various modes of depriving them of moisture for the purpose of chemical experiments, shall enter into the history of the physical and chemical properties of water.

SECTION V.

OF THE TRANSMISSION OF HEAT THROUGH BODIES.

It is a matter of every-day experience, that heat may be propagated from one part of a body to another, and also that this propagation takes place in unequal degrees with different bodies. Thus, if one extremity of a poker be heated to bright redness, the other will become so hot as to be intolerable to the hand; while, if a stick of the same length be inserted in the fire, the heated extremity may be completely burned off, without the farther extremity having its temperature raised in any remarkable degree. The extremity of a glass rod may be melted by the flame of a blowpipe, though held in the fingers scarcely an inch from the flame: but we shall find it difficult to melt the extremity of a silver wire, from the heat spreading itself generally through its mass, and elevating the temperature of its entire length almost to the same degree. Bodies which act like silver are said to conduct heat well, and are termed *conductors*. Bodies which intercept it, like wood or glass, are termed *non-conductors*. It is only a difference of degree, for there is no body which prevents totally the passage of heat across its mass.

The propagation of heat through a body, in virtue of its conducting power, is supposed to take place from particle to particle, precisely as, when we apply a heated to a cold ball of iron, the latter becomes warmed at its point of contact. If, in place of using balls of iron, cubical masses were employed, touching by their surfaces, the communication of heat would be much more rapid, from the greater number of points at which transmission could take place. In the interior of a body we should expect, therefore, to find the degree of approximation of the particles to have some influence on the rapidity of transmission, that is, on the conducting power, or, in other words, that the power of conducting heat should have some relation to the density and the cohesion of each body.

Many series of experiments have been made to determine the conducting power of different bodies. Such experiments may be arranged in a variety of ways. Thus, if a number of similar rods, of different substances, be coated to a certain distance from one extremity with wax, and then heat be applied to the other extremity, the wax will melt according as the temperature of each rod rises, from the transmission of the heat along it; and the length of the coating melted at the end of a certain time will be a measure of its conducting power. Another mode consists in forming the substances to be tried into disks, and, having placed a small morsel of phosphorus upon each, warming all equally by laying them on a heated surface. The phosphorus inflames first upon the disk which transmits most readily the heat, and on the other disks in the order of the conducting power of their substance. But such experiments are only useful in giving the order of conducting power in a general way, and are inapplicable to exact purposes.

The best results are those which have been obtained by Despretz, whose method was the following. All the bars used in his experiments were square prisms, and were all covered with the same black

varnish, in order that the loss of heat from their surface might be exactly similar. At every four inches of their length was a hole bored to half the depth of the bar, which was filled with oil or mercury, into which the bulb of a delicate thermometer dipped, so as at every instant to show the temperature of the bar at this series of points. By means of a lamp applied to one extremity of the bar, it was strongly heated, and the steadiness of the heat secured by finding the temperature of the thermometer nearest the lamp to be stationary for six hours, the usual time of an experiment. The temperature of the air of the room, which should scarcely at all vary during that time, is known by a thermometer.

After the bar has been heated for two or three hours, each thermometer arrives at a temperature which thenceforth continues the same as long as the source of heat is kept up. This temperature depends on the difference between the quantity of heat that is propagated along the bar from the lamp, and the quantity which is lost by cooling. The excess of the temperatures of the thermometers attached to the bar above the temperature of the room, forms, therefore, a series, the ratio of which depends upon the conducting power of the bar in a manner which, though not simply proportional, is easily deduced from it by calculation. By these principles, of which the theory was given by the celebrated Fourier, Despretz has deduced, from his experiments, the following conducting powers, gold being assumed as the standard for comparison.

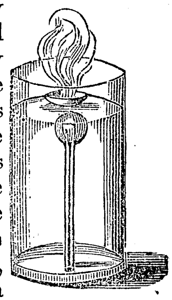
Gold	1000	Tin	304
Silver	973	Lead	180
Copper	898	Marble	23·6
Platinum	381	Porcelain	12·2
Iron	374	Fire clay	11·4
Zinc	363		

Although this series presents, when compared with the specific gravities, or other physical properties of these bodies, very great diversity, yet it is remarkable that the more expansible and more fusible metals, tin, lead, and zinc, are those which conduct heat worst. The position of platina is, however, quite anomalous, and must prevent any attempt at generalization.

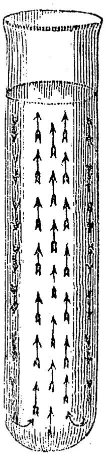
The difference of the conducting power of solid bodies is of daily utility in ordinary life, as well as in chemical operations. It is thus that substances of exactly the same temperature may produce quite opposite sensations to the hand. If we grasp in one hand a piece of metal, and in the other a piece of wood, both at 180°, the hand will be reddened and blistered by the former, but the latter will feel only moderately warm. If the metal and wood be both cooled to 32°, the former will feel intensely cold, but the latter scarcely at all so. In the first case, the metal gives out its heat to the hand, and in the second, abstracts it from the hand so rapidly that the nerves and circulation become acutely sensible of the change; but with the wood, from its low conducting power, the flow of heat takes place so gradually in each direction as almost to escape notice. The brickwork of a fireplace or of a furnace is for the purpose of keeping the heat generated by combustion from spreading to the surrounding bodies, and so being lost. It would be difficult to light

a fire in a massive metallic grate, for the heat would be so rapidly carried off by its conducting power, that the fuel, if not well lighted before being introduced, would be cooled down and extinguished.

Liquids conduct heat but very slowly; so slowly, that they were long considered to be true non-conductors. It is now satisfactorily proved, however, that they do conduct; and although no accurate numbers have been obtained, their power appears to be generally as their density; mercury being the best conductor, and alcohol and ether being the worst. This low conducting power may easily be demonstrated by experiment. Thus, if in a jar of water an air thermometer be inverted, so that its bulb shall be very near the surface, and the cup containing ether be laid floating on the water, as in the figure, the ether may be set on fire, and allowed to burn for a considerable time before any action on the thermometer becomes sensible, and even then the heat appears to have travelled rather by the solid material of the glass than by the water. If a little water be frozen in the bottom of a narrow tube, and a solid adherent piece of ice being so obtained, if more water be poured in so as to cover the ice to the depth of a few inches, on inclining the tube, and applying the flame of a lamp to the water near the surface, it may be kept boiling violently, and for a long time, before the ice begins to liquefy, and even then it is by the glass material of the tube that the heat is conveyed.



Notwithstanding such facts, it is still well known that heat may be communicated through large quantities of fluid, so that the mass shall be rapidly and uniformly heated. It occurs, then, not by conduction, but by diffusion; and the source of heat cannot be applied indifferently to any surface of the fluid, as it might be to a solid body, but must be applied underneath. When any portion of a liquid is heated, it expands, and, becoming specifically lighter, ascends in the mass, and is replaced by the colder and heavier portions, which, being in their turn heated, ascend also, and thus generate a circulating current of ascending warm, and descending cold liquid, as in the figure, by which every particle of the liquid is brought in succession into contact with the source of heat, and the resulting temperature quickly and uniformly gained.



In the case of water, and such liquids as have a point of maximum density, this communication of heat, by ascending and descending currents, occurs in the inverse order below that point. Thus, to warm water which is below 39·5°, the heat should be applied above, or to cool it farther the heat should be abstracted below. On this property depends the preservation of the lakes and rivers of these countries from total and eternal congelation. When the mass of water becomes cooled to 39·5°, the superficial layer becoming lighter as it cools more, prevents, by its non-conducting power, the farther abstraction of heat from the deeper portions; but when the warm air of spring plays on it, the heat is rapidly diffused from above downward, until the temperature of the entire mass is raised to 39·5°

In their mode of communicating heat, gases resemble liquids. Their true conducting power is quite insensible, but by the currents which are produced by the ascent of warm and the descent of cold particles, they abstract and communicate heat with great rapidity. The difference is easily felt by holding the hand first at the side and then over the flame of a candle, the distance being the same. In the latter case the great increase of heat arises from the ascending current of heated air, which does not affect the hand when at the side.

The non-conducting power of gases is practically of great importance. The different kinds of clothing owe their warmth to the fact that they prevent the heat of the body from escaping; this they effect not so much by the power of their proper solid substance, as by being of a loose and spongy texture, they imprison in their pores a quantity of air, which, not being able to form those continual currents, acts as a non-conductor. The more loose and spongy, therefore, the tissue of a cloth may be, the more air does it confine and the warmer it is. This is fully supported by the experiments of Rumford, who, having heated to the same degree a thermometer imbedded in the materials of which clothing is generally made, found that it cooled through 135° with

Air	in	576″	Raw silk	in	1284″
Fine lint	"	1032″	Beaver's fur	"	1296″
Cotton wool	"	1046″	Eider down	"	1305″
Sheep's wool	"	1118″	Hare's fur	"	1315″

When these bodies are tightly compressed, so as to diminish the quantity of air confined within their tissue, the power of retaining warmth diminishes in the same degree.

On standing before a fire, the influence of the heat is felt even at a considerable distance, although the air is, as has been just stated, so bad a conductor that the warmth cannot be ascribed to direct transmission through its mass; and since a current of air is passing to the fire in order to supply its conduction and produce the draught of the chimney, no heat can arrive at the body by the current from the fire. Also, if a heated iron ball be suspended in a room, it propagates heat in all directions, although the current of air which, so far as has been yet described, alone can convey any great quantity of heat, is directed only upward. Heat is therefore propagated by a third mode, distinct from diffusion and from combustion; and the heated body being supposed to emit actual quantities of heat in straight lines or rays from every point of its surface, this mode is termed *radiation*.

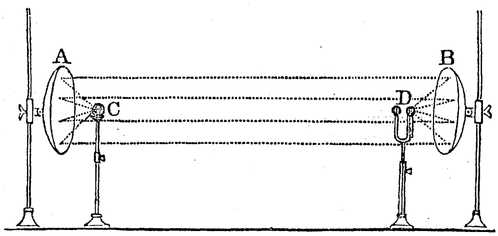
Radiation is remarkably distinct from conduction and diffusion in not requiring for its existence any material medium. On the contrary, the existence of any coherent substance in their path is an obstacle to the transmission of the rays of heat, and hence in most solids and liquids there is little heat transmitted by radiation, unless we look upon conduction as a kind of radiation from particle to particle in the interior of the mass, and it is only with gases that radiation is equal to what takes place in empty space. A heated body throws off rays of heat precisely as a luminous body throws off rays of light; and in every detail of physical constitution that

has yet been discussed, there exists a perfect similarity between heat and light in these radiant forms.

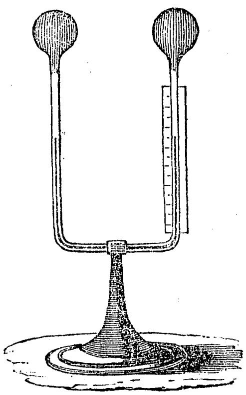
Different bodies radiate heat with different powers, which appear to depend more upon the mechanical nature of the surface than upon the internal constitution of the body. When any substance is interposed in the path of the rays of heat, these are either reflected, or are absorbed, or they pass through the body without loss. In general, all these effects are in part produced; that is to say, one portion of the incident rays will be transmitted, another portion reflected, and a third will disappear by being absorbed. There are thus in relation to radiant heat four qualities, which various substances possess in different degrees, the radiating, the absorbing, the reflecting, and the transmitting power.

The rays of heat may, like those of light, be concentrated by reflection or refraction. By the former mode, that originally used by Prevost and by Leslie, the properties of radiant heat may be demonstrated in a simple manner.

The form of apparatus generally employed for demonstrative experiments on radiant heat consists of reflecting mirrors of polished silvered copper, of a paraboloid form, A B; the property of this figure being that rays emanating from the focus of one mirror are reflected from it in parallel directions, and falling thus parallel upon the other, are brought to convergence in its focus. In this manner the heat radiating from a body may be concentrated upon a single point, and all its properties determined with great precision. Thus, a hot iron ball may be placed at a distance of a few feet from a bit of phosphorus for any length of time without affecting it; but if the hot ball be placed in the focus of one mirror, C, and the phosphorus in the focus of the other, D, this immediately begins to melt, and after a moment bursts into flame. If the hand be held in the focus, it feels hot; but, on moving it much nearer to the source of heat, the iron ball, it feels cooled. It is thus not by the direct conduction of the air, or by diffusion of warm currents, that the effects are caused, but from the radiation of heat in a form which, like light, admits of being reflected from polished surfaces, and concentrated upon a focus, and which will be found to follow the analogy of light through all its branches.

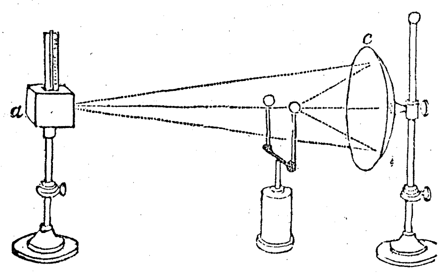


If a thermometer be placed in the focus of the mirror opposite the heated ball, it immediately indicates the rise of temperature, and may serve to measure it. But it is only the air thermometer which is delicate enough for



such experiments, and it is specially for this use that the differential air thermometer is constructed. One bulb being placed in the focus, the difference of temperature between the two bulbs is instantly shown; and it is thus also proved that the rise of temperature is local, that it is confined to the point where the rays of heat are brought to meet, for the instrument is insensible to every general change of temperature, no matter how extensive.

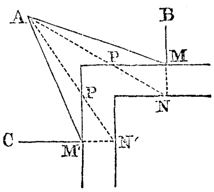
By means of this apparatus, the radiating and absorbing, as well as the reflecting and transmitting powers of bodies may be examined. The radiating power may be conveniently exhibited by filling a tin cube, *a*, with boiling water, and applying to the surfaces of the cube the bodies which are to be examined. Thus, one side being left brightly polished, another dimmed by being rubbed with sand paper, a third covered by paper, and the fourth being blacked by the smoke from a candle, each side, on being turned towards the mirror *c*, gives out a quantity of heat proportional to its radiating power, and this being reflected and brought to bear upon the thermometer in the focus, is measured by its indication. Leslie thus found the radiating power of the following surfaces to be relatively,



Lampblack	100	Plumbago	75
Writing paper	98	Tarnished lead	45
Crown glass	90	Clean lead	19
Ice	85	Polished iron	15
Red lead	80	Other bright metals	12

It is here evident that the radiating power is quite independent of the colour of the body, and that, in all cases, those bodies with bright metallic surfaces radiate least, the radiating power of lead being doubled by simply tarnishing its surface. It has been rendered probable, however, by recent observation, that it is not the degree of polishing of the surface which influences the radiating power, so much as the closeness and density of the exceedingly thin surface layer, on which the quantity of radiant heat depends. In the process of polishing, the surface of a metallic plate, particularly if it be rolled, is very much compressed, and in this state radiates in the lowest possible degree; but if, by rubbing with sand-paper, that dense film of compressed metal be removed, the softer material underneath radiates with nearly double the power. If a plate of silver be cast without being subjected to any pressure, the surface, although perfectly bright, radiates with a power of 22; but if it be dimmed by rubbing with sand-paper, the compression, even though so slight, diminishes the radiating power to 12. Substances which are highly elastic, as ivory, or very hard, as agate, radiate in the same degree, no matter what may be the rough or smooth condition of the surface.

That the texture of the surface should influence the radiating power is easily comprehended, when we know that it is not from the external surface, but from a little depth below it, that radiation actually takes place. If radiation were truly from the surface, every point of it emitting rays in all directions equally intense, there should occur inequalities in the temperature of the surrounding bodies of the most remarkable and intolerable kind. Thus, let us suppose two surfaces at right angles radiating heat, as, for instance, two surfaces of a red-hot poker. A body A, at a certain distance from the angle, should have its temperature raised much more than a body, B or C, directly opposite either side, for it should receive the rays A M and A M′ equally intense, while the bodies B and C should receive from the



same points only the rays B M or C M′. But the rays emanating not from the surface at M or M′, but from N′ and N, at some depth below, the oblique ray N A has to pass through so much a thicker stratum of solid matter from N to P than the direct ray from N to M, that the conjoint action of the two does no more than enable the surrounding bodies to attain an equable temperature. Bodies obliquely exposed to a flat radiating surface receive less heat; not that a smaller number of rays impinge upon them, but that a greater proportion of heat is lost in escaping from below the surface of the body.

The radiating powers of bodies are the foundation of numerous applications in the arts. Those bodies which radiate least cool slowest; and hence, if it be required to keep any material hot for a considerable time, it should be enclosed in a vessel with a bright metallic surface, that being the kind which retards most the escape of heat. If, on the contrary, the object be to diffuse heat, the best radiating surface should be made use of. It is thus that the tubes by which heated air, or water, or steam is supplied to buildings, for the purposes of warmth, should be bright and polished until they arrive at the precise locality where the heat is to be given out, but should there be painted with whitelead or lampblack, the surfaces by which the heat is most rapidly given out.

If two tin vessels, precisely similar in form, but one being painted and the other polished, be filled with warm water and placed in a cold room, that which is painted will cool more rapidly than the other, in consequence of its greater power of radiation. If the two vessels, when cold, be placed opposite a steady fire, the temperature of the water in that which is painted will be observed to rise more rapidly than that of the other; it will absorb the heat of the fire, precisely as it had given out the heat of the water, with most rapidity. The bodies, therefore, that radiate best, absorb heat, likewise, with greater power, and those which, when hot, cool most slowly, are those also which have least tendency to receive radiant heat.

The absorbing and radiating power may even be proved to be exactly proportioned to one another by the following experiment. A large differential thermometer is arranged, whose bulbs are chambers of considerable size, presenting large and equal plane surfaces on the sides that are towards each other. Of these, one is polished and the other coated. Midway between them is placed a canister having equal plane surfaces, facing each of the former respectively, and one polished, the other coated with the same pigment as before. This canister is filled with hot water, and is capable of turning on a vertical axis; thus the coated surface of the canister can be turned to the coated bulb or to the polished; in the former case, a great effect is produced upon the coated bulb, and a very small effect upon the plain; in the second case, the better radiating surface is directed to the worse absorbing one, and the worse radiating to the best absorbing, and the liquid in the tube remains perfectly stationary, establishing thereby the exact equality of the absorbing and radiating powers.

Although colour is without influence on the radiating power, it yet appears to influence the absorbing power in a remarkable degree. If pieces of cloth of various colours be laid upon snow, and exposed to the direct solar rays, that which is black will, by absorbing more heat, melt the snow away from under it, and sink deepest. White will sink least, and the others in the order of their depth of colour. It is, therefore, with reason that dark-coloured cloths are preferred for winter use, and light colours for summer. It is, however, to be

noticed, that it is only upon the absorption of those rays of heat which accompany rays of light that colour has this power.

The great difference of absorbing power of a blackened and of a metallic surface may easily be shown, by coating one bulb of a differential thermometer with silver leaf and blackening the other. When, with the same source of heat, the rays are received upon the silvered bulb, scarcely any rise of temperature can be observed; but when the blackened bulb is placed in the focus, the rise is much more than would have occurred with the thermometer in its ordinary condition of the bulb with a glass surface.

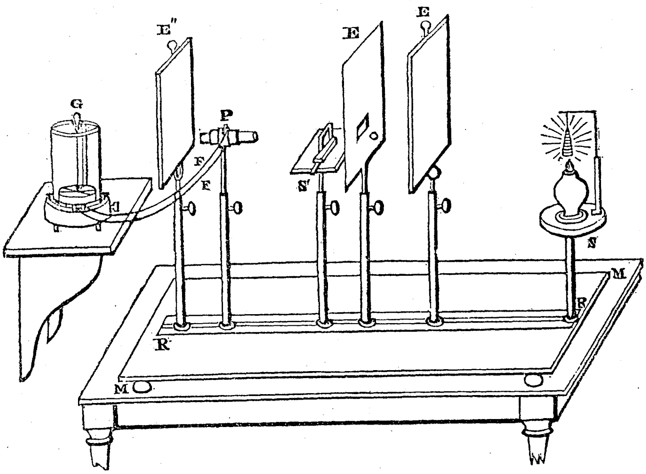
The mirrors which are used in those experiments do not become sensibly heated until after a long time; they absorb but very little heat: but if the surface of the mirror be smeared with glue, it loses to a great degree its power of reflecting; and having thus obtained an absorbing and radiating power, it very soon becomes warm. If it be coated with lampblack, its reflecting power vanishes, and its surface becomes highly absorbent. The reflecting property is therefore possessed by the surfaces of bodies in the inverse degree to the absorbing and radiating powers, and hence the best absorbers are those which reflect least.

The heat which is naturally associated with light in the sun's rays is capable of being so concentrated by reflection, that in the focus of a burning mirror, results equal to those of the most intense artificial heat may be produced. The heat of the sun's rays may also be concentrated by refraction, the heat accompanying the rays of light in their passage across lenses; hence the use of the burning glass. But when we thus come to discuss the property possessed by bodies of transmitting heat through their substance, it becomes necessary to look farther to the source and intimate structure of the heat. For the results which have as yet been described, we are indebted almost exclusively to Leslie, but the power of transmitting heat could only have led to the important consequences deduced from it by Forbes and Melloni more recently, when the advance of other sciences had placed at the disposal of the experimenter measures of temperature infinitely more sensible than any form of thermometer formerly in use.

It is by means of the thermo-multiplier and galvanometer that the effects of the transmission of heat require to be observed.

The apparatus employed by Melloni was, in its general arrangement, such as is represented in the subjoined figure.

On a steady table there rests a frame M M, along the middle of which a slip R R is cut, by which the various stands and supports may be moved back and forward, so as to vary their distances from each other. On the stand S is placed the source of heat; in the figure it is a coil of platina wire ignited by a spirit lamp; but the flame may be surrounded by a cylinder of blackened copper, or it may be a vessel of boiling water, or an argand or Locatelli lamp. The rays proceeding from it are received by the thermo-multiplier P, from which the wires F F convey the electricity generated to the galvanometer G, which for steadiness is placed at a distance, and on brackets secured against a wall. These parts, P and G, will be represented in full in the chapter on electricity. If it be required to study the action of a plate of any substance upon the rays of heat, the screen E is interposed, having an aperture O, somewhat smaller than the plate to be employed. This last is then supported immediately behind the aperture by means of the little frame S′, so that no heat can reach the thermo-multiplier unless after having passed through it. As it is of great importance to have the end of P farthest from the lamp uninfluenced by any disturbing causes, the screen E″ is placed immediately behind it, to protect it



from irregular radiation and from currents; and as the action of the heat upon the pile must be limited to the actual time of the experiment, the double screen E′ is interposed immediately next the lamp, and, being provided with a hinge, is raised or lowered at the moment when the rays of heat are to be allowed to pass or are to be intercepted.

The orifice of the thermo-multiplier is occasionally fitted with a conical tube of plated brass, for the purpose of collecting the rays of heat in greater number; but that is not often wanted.

The reflecting power of bodies has been exactly determined by Buff to be as follows. Of 100 rays incident at an angle of 60° from the perpendicular, there are reflected, by

Polished gold	76
" silver	62
" brass	62
Brass without polish	52
Polished brass varnished	41
Glass plate blackened on back	12
Looking-glass	20
Metal plate blackened	6

The power of a body to transmit heat is termed *transcalescence*, and of intercepting heat *intranscalescence*. These properties are totally independent of the power of transmitting light, as will be at once seen from the following table. Of 100 rays proceeding from the flame of an argand lamp, there are transmitted by

Rock salt	colourless	92	Glass coloured .	yellow	22
Calc spar	do.	62	Do. . . .	blue	21
Smoke topaz . . .	brown	57	Sulphuric ether .	colourless	21
Plate glass	colourless	40	Gypsum . . .	do.	20
White agate . . .	do.	35	Tourmaline . .	green	18
Glass coloured . . .	violet	34	Opaque glass . .	black	16
Do.	red	33	Citric acid . . .	colourless	15
Chromate of potash .	orange	33	Alcohol	do.	15
Borax	colourless	28	Alum	do.	12
Glass coloured . . .	green	23	Water	do.	11

Rock salt is thus the most transcalescent substance that has been

found. Glass arrests more than one half of all the heat which it receives, while colourless and transparent alum, and the most limpid water, arrest more of the heat which they receive than the deepest coloured glasses, or topaz, or quartz, so brown as to be quite opaque.

But not merely do different bodies act differently on rays proceeding from the same source, but the same body may allow the heat from one source to pass freely through its substance, and intercept partially or completely the heat radiating from another. Thus using, in his experiments, the heat emanating from five kinds of source, first, the argand lamp; second, the lamp of Locatelli, which is remarkable for the steadiness of its flame; third, a red-hot spiral of platina wire; fourth, a blackened copper plate heated to 734°; and, fifth, a blackened copper plate heated to 212° by boiling water, Melloni found the heat arising from these sources to be transmitted in the following proportion per cent.; the results with the argand lamp, having been given in the last table, are here omitted.

Substance.	Locatelli Lamp.	Ignited Platina.	Copper at 734°.	Copper at 212°.
Free radiation .	100	100	100	100
Rock salt . . .	92	92	92	92
Fluor spar . .	78	69	42	33
Calc spar . . .	39	28	6	0
Plate glass . .	39	24	6	0
Agate	23	11	2	0
Gypsum . . .	14	5	0	0
Alum	9	2	0	0
Ice	6	0	0	0

Rock salt is thus not only the most transcalescent body, but it is that which alone is equally transcalescent to heat of all temperatures. The rays of heat evidently acquire a greater power of transmissibility as the temperature of the source increases, and hence glass arrests scarcely any portion of the direct solar heat, while from the argand lamp it intercepts 47; from Locatelli's lamp, 61; from ignited platina, 72; from copper at 734°, 94; and from copper at 212°, 100 per cent. The action of these media upon radiant heat consists not merely in stopping a certain portion of it, but in separating it into two portions, physically distinct, of which one is capable of transmission, while the other is absorbed. Hence a second plate, of the same kind of substance, exerts but a very slight action upon the heat which has already passed through the first. Thus, though a plate of alum allows only 9 in 100 of the direct rays of the lamp to pass, yet it admits of the passage of 90 in 100 of rays which have already passed through a plate of the same substance; and calc spar, which transmits only $\frac{39}{100}$ of the direct heat, transmits 91 of that which had passed through alum, and 89 of that which had passed through gypsum. On the other hand, a green tourmaline, which transmitted 18 out of 100 rays directly incident upon it, intercepts $\frac{99}{100}$ of those which had previously passed through alum, but gives passage to $\frac{30}{100}$ of radiant heat which had passed through black glass.

The nature of the physical distinction between the intercepted and the transmitted portions of the heat is to be found in the differ

ent refrangibility of the rays of heat emanating from sources of various temperatures. If the rays of heat emanating from a lamp be incident upon a rock-salt prism, they will undergo refraction, subject to the same law of the sines as in the case of ordinary light, and there will be obtained a band or spectrum of rays from the lamp; the most refrangible will coincide with about the middle of the luminous spectrum, while the least refrangible will extend far beyond the limits of the least refrangible rays of light. The mean refrangibility of heat is therefore less than that of white light, and the length of its undulation, if that theory be adopted, longer in proportion.

If, now, the heat spectrum so obtained be examined by means of the media which have been already noticed, the explanation of the peculiarities in their action will be at once observed. Rock salt allows the rays of all degrees of refrangibility to permeate its mass; it is to heat what perfectly colourless glass is to white light; it acts equally on all portions of it. Alum stops all but the very least refrangible rays; it is to heat what ruby-coloured glass is to light, which allows only the rays of the least refrangible extremity of the spectrum to pass through. Glass, gypsum, and such bodies as give passage to the rays of least and of mean refrangibility, resemble those orange-coloured glasses which exclude the blue and violet rays of light, but admit the others.

After long search, Melloni at last found that by coating with soot the surface of a plate of rock salt, it became to heat what blue glass is to light; it excluded the rays of inferior refrangibility; and when a plate so prepared was combined with a plate of alum, all heat was intercepted, precisely as when, by laying a plate of blue and a plate of orange glass together, perfect opacity is produced, the one absorbing the portion of light which alone the other is capable of transmitting.

The rays of heat derived from sources of different temperatures are thus analogous to the rays of light of different colours. The higher the temperature of the source, the more does it resemble red light; the lower its temperature, the greater is its analogy with the violet rays. Hence alum absorbs all the heat from boiling water, but gives passage to that from the argand lamp; but alum is like a glass so deeply coloured red that it is almost opaque, and transmits only a small portion even of its own coloured light that may fall upon it.

When a ray of heat is incident upon a doubly-refracting substance, it follows precisely the same law as light, and is refracted doubly. In this case, also, the rays after emergence are found to be polarized in planes perpendicular to each other; and all those consequences of the mutual action of polarized rays which give rise to such magnificent phenomena of colours in the case of light, must occur with heat, and be made sensible if our organs or our instruments were of a construction suitable for their appreciation. As yet, however, the fact which alone remains wanting towards a physical theory of heat has not been observed—that of interference; up to the present time, the actual production of cold by the combined action of two rays of heat has not been seen; but the closeness of the analogy, which in this case alone requires additional observation between light and heat, is so remarkable, that we can have little hesitation in referring these agents, in their radiant form, to the same kind of physical arrangement.

There is no difficulty in conceiving radiant heat to consist in vibrations of the same ethereal medium which produces light, and in considering that the difference

between heat and light should be in the magnitude of the vibrations, and the consequent refrangibility of their rays. On the contrary, it is not reasonable to suppose, that while we are conscious of the waves in air, although they may vary in length from 32 feet to $\frac{1}{30}$ of an inch, the limits of our sensibility to the ethereal waves should be so narrow that the shortest (violet) is to the longest (red) as 60 to 38; it is more consonant to our idea of the various and beautiful uses to which every object of creation is made subservient, to believe that, while the waves within these limits produce upon the eye the sensation of coloured light, another range of lengths, greater than those of light, should give to our organs the sensation of radiant heat; and that a third order of vibration, still shorter, and more refrangible even than violet light, is capable of acting upon the elementary constituents of bodies, and constitute the chemical rays. The coexistence of these three kinds of rays in solar light is an argument remarkably in favour of this view; for we can well imagine that, by whatever means the sun communicates to the ethereal expanse the vibrations of various lengths which constitute the rays of light, that vibrations of other magnitudes, greater or less, should be at the same time produced; and thus the light, which exhibits to us the beauty of the external world, be accompanied by the heating power which animates all living nature, and without which the universe would be a tenantless and barren void.

These arguments, however natural, and in appearance sound, are met by facts which, if not positive against light and heat differing only in the length of the waves by which they are produced, are at least of so much importance as to deserve attentive study. If it were so, then the heating rays of the spectrum should be thrown always below the coloured space, being less refrangible; and it is found that, with a flint glass prism, the greatest heat is produced outside the visible confines of the spectrum at the limit of the red light. This is, however, only accidental, from the nature of the prism; for if a prism of crown glass be employed, the rays of heat are collected in the middle of the red space: with a prism of sulphuric acid, in the orange; and by a prism of oil of turpentine or water, they may be collected into the centre of the yellow light.

The rays of heat, therefore, although generally less refrangible than those of light, are still not necessarily, or even always so. There is distributed over the entire visible spectrum a heating spectrum, which has its peculiar point of greatest energy, and which may be refracted more or less quite independently of the luminous space, and may be brought to overlap it at either end, or to lie evenly upon it. The ethereal medium, if it be the means of transmitting radiant heat, must be capable of two distinct methods of vibration, by which rays of equal refrangibilities, but totally different properties, may be produced.

The physical independence of solar light and heat was beautifully shown by Melloni, who, using quartz and black mica, perfectly opaque, upon the one hand, and rock salt made perfectly opaque by soot upon the other, obtained radiant heat of all refrangibilities totally free from light; and on the other hand, by combining a plate of alum with a glass coloured green by oxide of copper, he obtained a brilliant beam of light, which, when concentrated by a lens upon the most delicate thermoscope he could apply, exhibited no trace of any heating power whatsoever.

An interesting property of radiant heat, and one which shows the remarkable distinction between it and light in a very evident manner, is, that the heat may change its degree of refrangibility; and hence, if it be vibrations, one wave may break it up into several, or several smaller waves may unite to form one. The light of the sun, deprived of all the more refrangible rays by passage through a plate of alum, may be received on a blackened surface, the temperature of which will be thus elevated, and which, in turn, will become a source of radiant heat. But the heat so radiated is found to have totally changed its properties; it can no longer pass through alum; it has passed from the state of heat of the lowest to the state of heat of the highest refrangibility. In like manner, if the most refrangible rays emanating from a source at 212° be concentrated by a rock-salt lens, and brought to act on a small surface, they may raise the temperature of this surface above 212°, and radiate from thence in a less refrangible condition than before. The parallel case to this has never been found with light. Red light has never changed into blue, nor violet into orange; and there must be in the physical theory

of radiant heat some general principle of so high an order, that the physical optics of the present day is but a particular case of it.

This change of radiant heat from one degree of refrangibility to another occurs in nature very often, and is the source of some remarkable phenomena. Thus the heat of the sun's rays, being of low refrangibility from their intensely-heated source, is transmitted easily by ice or snow, and hence a layer of snow upon a field, exposed even to the powerful action of the sun, is but slowly melted; if, however, a dark-coloured object, as a branch of a tree, be laid upon the surface, it absorbs the solar heat, and becoming a source of radiation of heat of great refrangibility, which the snow absorbs completely, this is melted under the stick, which sinks and gradually disappears beneath the surface. The earlier melting of snow upon the branches and round the stems of plants, which was supposed to demonstrate a kind of natural warmth belonging to the living vegetable, arises from this merely physical conversion.

From this results also the influence of colour on the power of bodies to absorb the heat of the sun or of a fire; the strips of coloured cloth (page 97) melted the snow beneath them, not merely because they absorbed more heat in proportion to the depth of colour, but because they in that proportion possessed the property of changing the heat, which would be transmitted into the heat which would be absorbed by the snow on which they rested.

The construction of a theory of heat would be, even were an undulatory hypothesis adopted for its radiant form, involved in difficulties which may require many years of research to render them even clearly understood. The relation between radiation and conduction; the connexion between specific and latent heat; the laws of cohesive force against which heat acts in causing the expansion of a body, will all require to be comprehended within the folds of whatever principle shall hereafter be made the basis of thermotics. But it is no disrespect to the illustrious names that have been connected with speculations on this subject, to conclude, that none of the views brought forward appear positive or clear enough to be described in a work of an elementary nature like the present.

SECTION VI.

OF THE COOLING OF BODIES.

Bodies at an elevated temperature are capable of giving out the heat which they contain by every method by which, when cold, they become heated at the expense of the surrounding warmer bodies. Cooling may occur, therefore, by *contact* or by *radiation*. The rapidity of cooling by the immediate contact of the hotter with the colder body depends on the degree of intimacy of the contact, and on the conducting powers of the bodies. Thus solids, which merely touch at a few points, communicate their relative temperatures but very slowly, while with liquids or gases which may mix completely with each other, the establishment of a uniform temperature is almost instantaneous. The colder body becomes heated to the original temperature of the hotter only when there is a continual supply of heat to maintain that temperature, as in a furnace; in other cases the hotter body cools in proportion as the colder becomes warm, and the resulting temperature depends on the specific heat of each, as has been described, page 62. In determining, therefore, the temperature of a body by a thermometer, it must not be forgotten that the thermometer, in becoming hot, cools the body, so that, unless there be a continuous source of heat, the true temperature of a body is never given by the instrument. Where the substances, being solid, can only come into external contact, the rapidity with which heat passes from one to the other depends upon their conducting power; thus, a cold brick may be laid upon a heated brick for a considerable time without much heat changing place, but a plate of red-hot iron laid

upon a plate of cold iron, abandons its excess of temperature so rapidly, that a mean temperature is attained by both in a very short time.

The cooling of bodies by radiation is governed by the principle that all bodies in nature are in a continual state of interchange of heat; no matter how hot or how cold a body may be, it is constantly giving out radiant heat to other bodies, and receiving in exchange, and absorbing the heat which radiates from them. The quantity of heat thus radiated depends on the temperature of the body; the higher this is, the greater quantity of heat is thrown off; the lower the temperature, the less heat does a body radiate in a certain time. Hence, if we conceive a ball heated to redness, and suspended in the centre of a number of similar but colder balls, each will radiate and absorb, but the hotter ball will give out more than it can gain in return, and will hence cool, while the surrounding colder bodies, absorbing more of the radiant heat than they return, will have their temperature raised. Every body in nature, therefore, no matter how its temperature may, by peculiar or local means, be elevated or depressed, tends ultimately to an equilibrium with all the neighbouring bodies; and hence, the instant we remove a substance from our furnaces or freezing mixtures, it begins to cool or to become less cold. This principle explains, in a very perfect manner, a singular but instructive experiment which may be made with the concave mirror apparatus described, page 95. In the ordinary form, the thermometer and the heated ball tend, by radiation, to assume a common temperature, and the thermometer, being the colder body, becomes heated; but if, in place of the heated iron ball, a mass of ice be substituted, the temperature of the thermometer in the focus of the opposite mirror immediately sinks below that of the surrounding air. The explanation consists simply in the fact that the thermometer is now the hotter body, and hence, giving out to the ice more heat than the ice gives back, has its temperature reduced. At first this effect appeared to demonstrate the existence of rays of cold, which were reflected, radiated, and absorbed like rays of heat.

In this principle of the uniformity of temperature being sustained by the equivalent radiation and absorption of the bodies at the surface of the earth, we find the solution of many interesting natural phenomena. The production of dew and frost are to be thus accounted for. In the absence of the sun, the surface of the earth losing by radiation a great quantity of heat, would have its temperature considerably lowered, were it not that the canopy of clouds which generally lies above it radiate in return, and thus maintains the temperature almost the same. If, then, the clouds be absent, all the heat radiated by the earth is lost in the planetary spaces, and the temperature of its surface brought many degrees below that of the atmosphere. The stratum of air which lies in contact with the surface of the ground is then cooled by contact, and a portion of the watery vapour which it had possessed in its elastic form is deposited as liquid water. If the temperature of the air be itself low, and the night very clear, the cooling may proceed so far that the drops of dew at the moment of their deposition shall be frozen, and thus form frost. The truth of this explanation is demonstrated by

the fact that it is only on the surface of good radiators, and during clear starlit nights, that dew or frost is found. If a plate of polished metal be laid on the centre of a rough board, and exposed to the air of a frosty night, the rough surface will be found in the morning covered with copious frost, but on the bright metal no trace will be deposited. It is thus that, by lightly covering a thin layer of water with straw to increase the radiating power, a sheet of ice may be obtained in a single night between the tropics, where the actual temperature of the air may have continued far above the freezing point. That the cooling effect is produced by the loss of heat in its radiant form, and not by the contact or diffusion of the particles of the air, may be proved by the interposition of a screen of any substance which intercepts the passage of radiant heat, when the deposition of dew or frost instantly ceases, and the surface cools no more. Thus plants are protected by mats from the frost of spring and autumn, and thus the screen of snow, which covers the surface in the depth of winter, prevents the loss of heat from the soil below, and favours the vegetation of the seed.

The rapidity of cooling depends upon the difference of tempera ture of the radiating bodies, but it is not proportional to this difference except within a very narrow range of temperature. Newton having experimented only within that limit, announced that law as general; but the establishment of the true law is due to Petit and Dulong. It is, that the rapidity with which a body cools, for a constant excess of temperature, increases in a geometrical proportion, of which the ratio is 1·161, when the temperatures increase in an arithmetical proportion. Bodies at moderately high temperatures cool, therefore, much more rapidly than they should do by Newton's law.

The heat, by means of which we produce a rise of temperature, or any other of the effects which have been described, may be derived from any one of a variety of sources. To the earth at large the sun is the source of warmth; and by his varying position in the heavens, by which his rays strike upon the surface with different inclinations, and, passing through the different thicknesses of atmosphere, undergo absorption to a variable amount, the change of seasons as to temperature is produced; and the alternation of vital activity and torpor which characterizes the vegetable world, and a great portion of the animal creation, is occasioned. Although at the surface the temperature of the earth is solely dependant upon the radiating power of the sun, yet it is found that it contains within itself a source of heat, which, in ages excessively remote, must have retained the general mass of all constituents of the mineral globe in igneous liquefaction. In fact, if we dig below the surface of the earth, we arrive, at a depth of about forty feet, at a layer of which the temperature is in winter and in summer exactly the same. It is termed the stratum of invariable temperature, and is in general of the mean temperature of the place; that is, the temperature of the surface falls in winter as much below that of the invariable stratum, as in summer it is raised above it by the excessive action of the solar rays. The heat of the sun, falling upon the surface, is transmitted inward in virtue of the conducting power of the ground; and thus, each summer, a thin layer of elevated temperature moves inward, those of successive summers being separated from each other by the intervening colder shell, which marks the period of diminished heat in winter, until they mix and confound themselves in the layer of constant temperature, below which the influence of the sun is felt no more. But, on descending beyond this depth, the temperature steadily increases, and, although subject to irregularities consequent on the different conducting powers of the rocks of different countries, the augmentation is in general about one degree for every forty-two feet, or about 120° for every mile. At a depth of two miles, therefore, water could not exist as a liquid, unless from the great pressure to which it would

be subjected: at four miles' depth tin and bismuth would naturally be liquid; and at five miles, lead. At a depth of thirty miles the temperature would be so high as to melt iron; and still more easily, almost without exception, the rocks, which constitute the solid earth which we inhabit. The central heat, therefore, although insensible at the surface, is still, there is every reason to believe, in violent activity at a small depth below: we live upon a pellicle of solid crystalline rocks, with which the melted mass has become skinned over, and which extends but to $\frac{1}{140}$ of the distance to the centre. Hence we can well imagine, that in many places where orifices or cracks in this solid crust might form, violent manifestations of the internal fire should be produced, and the magnificent phenomena of volcanoes and earthquakes should thus arise.

For artificial purposes, the source of heat is generally chemical combination. The details of this mode of generating heat will require to be carefully and minutely considered hereafter, under the heads of Combustion, and the Relations of Heat to Chemical Affinity. By mechanical causes, as percussion and friction, heat may also be set free; but such cases arise from a change in the specific heat of the bodies before and after the mechanical action; and hence, although once considered as influencing our ideas of the nature of heat, do not now require special notice. A very interesting source of heat consists in the respiration of certain kinds of animals, and constitutes an important branch of chemical physiology, which shall be discussed in its proper place: and, finally, one of the most remarkable sources of heat is to be found in the properties of electricity, in its various forms; and to the description of this interesting and important agent we shall now proceed.

CHAPTER IV.

OF ELECTRICITY CONSIDERED AS CHARACTERIZING CHEMICAL SUBSTANCES.

Among the various forces which concur to the production of natural phenomena, there are few whose agencies are more remarkable or more general than those of electricity; and so intimately does it appear to be connected with chemical action, becoming sensible in all cases of union or decomposition, and being even developed in a degree proportional to their amount, that the most eminent philosophers have not hesitated to consider electrical and chemical agencies as being, if not identical, at least intimately connected with each other.

It is not the object of this work to enter into the minute description of electrical phenomena, nor to attempt the detailed discussion of their causes; as for a complete examination of the subject, it must be considered as one, and certainly not one of the least extensive branches of natural philosophy; it is only with regard to the influence which electricity exercises in the operations and the theory of chemistry, and the means which the electrical properties of bodies afford for their recognition, that it requires notice here; and hence, although it is necessary to describe the peculiar origin and characters of each form which electricity assumes, yet that shall be accomplished within the shortest limits that are consistent with the importance of this branch of science. In the present chapter the subject will be studied in its general history, and considered as affording useful characteristics of substances, the properties of which we have to learn; and in a future place the influence which it exercises upon chemical affinity, and the opinions which have been advanced concerning its relation to purely chemical forces, shall be carefully discussed.

Of the true nature of electricity nothing is positively known; whether it be a mere property of matter like attraction or cohesion, a mere force acting independently of all interposed material, or whether, like light, it consists in the undulations of an ethereal medium fill-

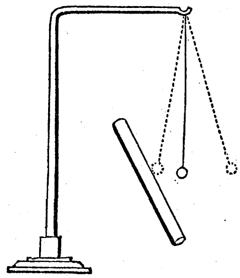
ing space, cannot be determined. Indeed, the ordinary views of its nature consist in supposing the existence of one or of two fluids of electricity, of exceeding tenuity and of perfect elasticity; and that, according as ordinary bodies were supposed to contain more or less of these fluids of electricity, they acquired or lost the properties of electrical excitation. Of these opinions it is exceedingly difficult to say which is the more reasonable or more consonant to experimental truth, so far as the explanation of phenomena is concerned; but no positive evidence has ever been obtained of the existence of such an electric fluid: it has never been found capable of being separated from the ordinary particles of matter, of which it appears always as an additional property assumed under peculiar circumstances, and not as a superadded constituent. I consequently incline to the idea that, in the phenomena of electricity, we have exhibited only the results of new mechanical conditions of the ordinary particles of matter, produced by the action of forces which may be called into play in a variety of ways, and which may be either totally new forces which are first generated at the time, or modifications of the forces of gravity and cohesion which exist already. But, although such may be the true condition of the electric properties of bodies, yet such views are far too abstract and indefinite to be as yet carried out into the detailed explanation of experiments; and hence, in the present chapter, I shall adopt the language of that view, which has been so long in use as to have become incorporated with science, and speak of an electric fluid uniting with or separating from ordinary bodies, without being considered as at all believing in its actual existence.

This electric fluid, whether it be looked upon as of one or of two kinds, may, like air or water, be examined in a state of rest or in motion; and the science of electricity may be thus divided into electrodynamics and electrostatics. The electricity generated by friction, or by change of state of aggregation, is ranked under the latter head; while the effects of electricity in motion are found to include the phenomena of magnetism, of galvanism, and their relations to each other, electro-magnetism and magneto-electricity, and also those of the electricity produced by a change of temperature in bodies. Under these heads, therefore, the subject will be treated of at present.

SECTION I.

OF STATICAL ELECTRICITY.

Electricity, in its statical condition, may be evolved in various ways, of which one of the most remarkable, and that most commonly employed, is friction. If a piece of silk, or a handkerchief, warm and dry, be rubbed briskly against the surface of a dry glass rod, a peculiar odour will become manifest; and in the dark, the surface of the glass rod will appear covered with a peculiar phosphorescent glow. If the rod be brought near the cheek, a sensation as if a spider's web had been drawn across the face will be felt; and on approaching to the rod, as in the figure, any very light bodies, as a silk thread, a feather, balls of elder pith, or little bits of paper, they



will suddenly spring towards the rod, and become attached to it for a moment; after which they will spring from it, and fall away with equal power, assuming the positions of the dotted lines. The rod which has acquired these properties is said to have been electrified by friction with the silk handkerchief; it has become excited, and the phenomena produced are known; the phosphorescent appearance, as the electrical light; the motion to and from the rod by the light bodies, as electrical attraction and repulsion; in which also, acting on the minute down of the cheek, the sensation above described has its source. It is not alone by rubbing together silk and glass that these phenomena may be produced; two pieces of silk, by their mutual friction, become electric also, particularly if they be of different colours; thus, on laying flat together slips of black and of white riband, and drawing them smartly through the fingers, each will attract the feathers or pith balls; and being both light bodies, they will also attract each other. A piece of sealing-wax, or any other resinous body, when rubbed with flannel or a woollen cloth, becomes similarly excited. Sulphur and amber, in which last, indeed, the property was first discovered, and from the Greek name of which, *ηλεκτρον*, the science electricity has its name, assume this excited state with remarkable facility and power.

It is not every substance which may be thus electrified by friction, and even the same substance may often become incapable of being excited; thus, if the silk or flannel be not completely dry, if the glass rod be damp, no electric properties can be conferred upon them. But it matters not how much care we use in drying a metallic surface which rests upon the ground, or which we support by the hand, it cannot be electrically excited by any amount of friction. Such a body is termed a *non-electric;* dry glass, resin, sulphur, silk, &c., being called *electrics*. Excitation may therefore be produced by rubbing together two electrics, but by the friction of *non-electrics* no electrical effects can be observed. This distinction is, however, not real; it arises from the construction of the apparatus; for if, in place of resting the metallic rod or plate upon the ground, or grasping it in the hand, we support it on a piece of sealing-wax, or hold it by a glass or resinous handle, it becomes, when rubbed with the silk, as highly electrified as any of the electrics; and in this way, by suitable arrangement of supports, all bodies in nature may be made to assume electric properties by friction.

To account for this diversity of character, bodies are supposed to retain the electric fluid upon their surface with different degrees of power, according to their nature. When by friction electricity has been accumulated upon the surface of a glass rod, it being a highly elastic fluid, its particles repel each other, and tend, consequently, to escape from the limited space which it occupies, precisely as air tends to escape from a vessel into which it has been powerfully condensed. Glass, resin, sulphur, amber, silk, flannel, and such bodies, do not allow of such escape of the electricity, and it is hence

retained in its elastic form upon their surface, and produces all the effects of excitation. They are *electrics* because they are *non-conductors* of electricity. But such is the molecular constitution of the metals, that they allow of the escape of all that is set free upon their surface, unless its passage away to other bodies is intercepted by the interposition of some non-conducting substance. A metal is thus a *non-electric* because it is a *conductor* of electricity; and when, by supporting it upon a non-conductor, we oblige it to retain its charge of electricity, it is said to be *insulated.* Ice is a non-conductor of electricity, and by rubbing a stick of ice it becomes excited; but it must not melt upon the surface, for liquid water, although inferior to the metals in conducting power, is yet so excellent a conductor, that it allows the electricity which we might develop to pass totally away. Hence the necessity of drying carefully the substances which are, by their friction, to produce the electricity, and also the reason that insulating bodies must be kept free from damp; for if the thinnest layer of moisture be deposited upon their surface, the electricity will instantly escape by the path so opened for it.

The conducting powers of bodies have as yet been scarcely ascertained with accuracy enough to justify their being expressed in numbers, at least for the non-metallic bodies. The general order appears to be, commencing with the best insulators or worst conductors:

Dry air.	Glass.	Strong acids.
Shell-lac.	Spermaceti.	Fused saline bodies.
Resins.	Damp organic bodies.	Charcoal.
Oil of turpentine.	Damp air.	Metals.
Sulphur.	Water.	

The worst metallic conductor is many thousand times better than water, and by the following method an idea of their relative power may be formed. A wire, across which an electric discharge is passed, becomes heated in proportion to the resistance offered to the motion of the electricity, and therefore the rise of temperature is inversely proportional to the conducting power. By such experiments Harris found that, with

	The Heat evolved.	The conducting Power.
Silver	6	120
Copper	6	120
Gold	9	80
Zinc	18	40
Platinum	30	24
Iron	30	24
Tin	36	20
Lead	72	12

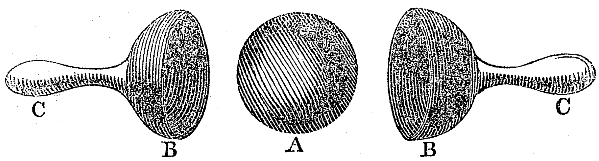
These numbers are merely comparative, and can only be looked upon as approximations.

The difference of the conducting power explains the fact that, when we excite by friction the surface of a glass plate or rod, it is only at the points actually rubbed that electricity at first appears, and it requires considerable time to creep over the other portions; but on exciting an insulated metallic rod or plate, no matter how ex-

tensive or how long, the electricity, when evolved by friction at a single spot, appears uniformly distributed over the entire. Hence, also, a spark may be obtained by electricity passing instantly along a great extent of metal surface, but is interrupted by a narrow interval filled by any non-conducting matter.

The rapidity with which the electric impulse is propagated has been examined by Wheatstone in a very ingenious manner, the details of which could not be well introduced here, but which enabled him to determine an interval of the $\frac{1}{152000}$ of a second; he found that the impulse of the shock of a Leyden jar is transmitted from each end of an interposed wire, and arrives latest at the centre, so far appearing favourable to the idea of the existence of two fluids rather than of only one, and that the velocity of transmission of this impulse is greater than that with which light passes through the planetary space, that is, at the rate of more than 195,000 miles in a second of time.

The electricity, when thus evolved, accumulates upon the surface of the body, not penetrating to any appreciable depth, but forming a layer of fluid, which by its elasticity, and hence expansive power, tends constantly to break away and pass to other bodies which are not excited. It thus passing through air produces the electric spark, and is accompanied by a snapping report. The tendency to escape under the form of the spark depends upon the thickness of the layer of electricity, and is accurately proportional to its square; so that if we excite a brass ball with double or treble the quantity of electricity, the force of the electricity to pass away will be quadrupled, or increased ninefold. Hence it requires exceedingly good insulation to retain electricity of great intensity.



These principles may be easily demonstrated by means of the apparatus in the figure. A is a hollow sphere of some conducting substance, and B B are hemispheres of gilt paper or thin metallic foil, which, when closed upon the globe, cover its surface accurately. They are provided with insulating handles, C C. The hemispheres being placed on the globe, if the whole be excited by friction or by a spark from the machine, the electricity will be found uniformly diffused over the whole external surface; and if the hemispheres be suddenly removed by means of the handles, the globe A will remain totally deprived of its electricity, which will be found all collected on the surfaces of B and B; but it will be no longer uniformly spread; its intensity will be found much greater on and near the edges of the hemispheres, and towards the centres of the surfaces the signs of excitation will be extremely feeble.

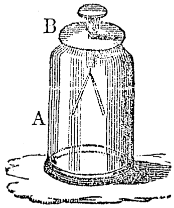
The form of a body has a remarkable influence upon the manner in which the electricity is distributed upon its surface. In a sphere the layer is everywhere of equal thickness, but in an elongated body

it accumulates more at the extremities of the longest axis. Hence on a wire or a needle, the electricity is accumulated almost exclusively on the ends; and even though the total quantity of electricity may not be large, it is there so thickly heaped that it breaks off and rapidly escapes. Hence electrical apparatus should be completely smooth except where a point or projection is intentionally attached, and many remarkable experiments are founded upon the escape of electricity from points. Electricity is not merely prevented from accumulating upon a pointed body itself, but it cannot collect upon any surface near it, the point abstracting the electricity. Thus, a point held near to the excited glass tube used in the experiments first described may prevent the attraction of the light bodies, which demonstrates its excited state, by concentrating all the action upon itself. The detailed theory of this power of points to dissipate their own electricity and to absorb that of other bodies, will be hereafter fully noticed; at present it is sufficient to refer it to the thickness and high elasticity of the layer of electric fluid which forms upon them.

It has been already stated that, when two slips of silk riband are excited by rubbing against each other, the electricity appeared to be equally evolved upon each. This occurs in all cases of excitation by means of friction. Thus, when silk and glass are rubbed together, the silk acquires as much electricity as the glass, but by the silk being held in the hand, the electricity escapes by the dampness which is always present, and is lost. If, however, the silk be insulated; if a disk of dry wood covered with some folds of silk be held upon an insulating handle, and rubbed against a similar disk of glass, then the same phenomena are produced in an equal degree by both. The attraction and repulsion of light bodies, the odour and the phosphorescence belong to both, and thus in every case where bodies are rubbed together, the excitation is completely mutual. There is, however, a profound and curious difference between the two conditions: separately they attract and repel other bodies exactly in the same way; together they produce neither attraction nor repulsion: separately they may manifest the most remarkable evidence of tension, giving sparks and shocks; but when combined, all signs of free electricity are lost, and the body on which they are collected appears as destitute of excitation as if the power had never been called into existence. The states of the two bodies are therefore so far opposed that they may interfere; and as from the action of two lights there may be produced total darkness, so from the coalition of the excitation of the two bodies which had been rubbed together, absolute indifference may result.

This neutralizing power of the excitation of each body for that of the other may be shown by very simple means. If a feather be suspended by a silken string, and upon the one side there be presented to it the disk of glass, and upon the other the disk of silk, which had been rubbed together, it may be brought to remain, by managing the distance, perfectly at rest. If there be the glass alone, it instantly attracts the feather; the silk alone acts in the same way; but no matter how strong the power of each may be, when at equal distances the feather remains indifferent to both. In order, however, to obtain perfect demonstration of this principle, it is useful to examine it by means of more exact instruments than the feather or other light bodies, which hitherto have been sufficient, and for this purpose the gold-leaf *electroscope* is best adapted: deferring the description of its principle to another

place, I shall here only notice its construction and the indications which it gives



A glass jar, A, is closed at the top by a metallic (brass) plate, B, to which are attached below, by a wire, two slips of gold leaf, lying, when unexcited, flat on one another, and reaching below the middle of the jar. The jar rests on a wooden or metal foot, with which are connected two slips of tin foil, applied to the inside of the glass, and rising so far that the gold leaves, on opening out, may come into contact with them. When this occurs there is evidently a free conducting medium from the upper metallic plate to the ground; but, except when the gold leaves touch the slips of tin foil, the cap and leaves are perfectly insulated, if the instrument be kept dry. When this electroscope is brought near to an excited body, the gold leaves diverge, and remain so, in the position of the figure, as long as the excited body be kept near. But if the instrument be not touched, the leaves collapse on its removal, and all remains indifferent, as it had been before. By the divergence of the gold leaves, therefore, the existence of free electricity acting on the electroscope is made known.

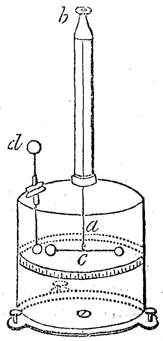
No matter what may be the nature of the excited body acting on this instrument, it gives the same indication of its presence, but when exposed to the action of the two bodies which had been rubbed together, the gold leaves remain quiescent. If they be made to separate by the influence of the glass, and the excited silk be then slowly approximated, the divergence gradually diminishes, until at last the leaves lie close together. If the silk be then brought still nearer, there is a new divergence, but it is due to the excess of power of the silk after the neutralization of the glass. On removing either of the excited bodies when the instrument is in the neutralized condition, the leaves diverge, from that remaining being free to act. Not merely is the excitation assumed by the two bodies immediately rubbed together, of these opposite kinds, but it may be shown that this peculiar power may exist in the conditions of two bodies rubbed by a third, as if a glass be rubbed with silk, and an insulated metal rod be likewise excited by rubbing with silk, the glass and metal rod assume electricities which destroy each other, or the silk is related to the metal as the glass had been to the silk. Bodies rubbed by different other substances are also so circumstanced; if a stick of sealing-wax be rubbed by flannel, it will assume opposite excitation to that of glass when rubbed with silk, and would counteract its influence; and, consequently, the condition of the flannel in the one case, and the silk in the other, would be opposite also. This assumption of opposite states of excitation may be caused by trifling mechanical conditions: thus, if smooth glass and muffed glass be both rubbed with silk, they become oppositely electrified; and two pieces of silk, which differ markedly in colour, neutralize each other when electrified by their mutual friction. The peculiar characters of these two forms of excitation extend, however, much farther than the principle of mutual destruction. If we hang by a dry silk thread, varnished with shell-lac in order to render it a better insulator, a little cylinder of gilt paper, and bring near it an excited body, the cylinder is attracted, and moves towards the body until it touches, when it is immediately and forcibly repelled. It has by contact participated in the state of excitation of the body, and, when that is so, they mutually repel each other. In all cases, bodies which are in the same electrical condition repel each other; and it is thus that the gold leaves of the electroscope become an index of any electricity which may be present; for as both slips of leaf are necessarily excited in the same way, they repel each other, and, consequently, they diverge.

If, now, the insulated gilt paper cylinder which has been, as above described, repelled by the glass rod, after having shared its electricity, be brought near the silk against which the glass rod had been rubbed, or to any body which is in the same state of excitation as the silk, attraction will ensue, and this will be found more powerful than if the body had previously been neutral. If two such gilt paper cylinders be touched, both with the glass rod or both with the silken disk, they will repel each other; but if one be touched with the glass and the other by the silk, they will attract each other, and move until they touch, when the states of excitation neutralize each other, and they become inactive.

When bodies are rubbed together, therefore, they become electric, and with such properties, that while each when separate gives signs of powerful excitation, together they destroy each other's power. Bodies when thus oppositely electrified attract each other;

bodies which are excited in the same manner repel each other; and these attractions and repulsions arise from the exertion of a force which, like that of gravitation, diminishes in intensity according as the square of the distance between the bodies becomes greater.

This law, which is of the greatest importance for the theory of electricity, was discovered by Coulomb by means of the *torsion electrometer.* The gold-leaf apparatus, though exceedingly sensible as a test of the presence of free electricity, is yet not susceptible of being used to measure its amount. It is an *electroscope,* but not an *electrometer.* The torsion balance of Coulomb consists of a glass drum, *a*, on the centre of which rises a glass tube, *b*, to the height of one or two feet. From the top of this tube is hung, by a fine thread of glass or of cocoon silk, a very light wooden beam, *c*, to which is attached at one end a ball of dry elder pith, and at the other a piece of gilt paper, which serves as a counterpoise, and by its surface prevents irregular motions of the beam. The pith ball is usually gilt, to give it a more uniform surface. In the top of the drum there is an aperture, by means of which a second gilt pith ball, *d*, may be introduced, and made to touch that of the balance; and around the centre of the drum is fixed a scale of degrees, by which the angular distance to which the balls separate after repulsion may be measured. Now let us suppose that, by touching the second, or, as it is called, the carrying ball, to an excited body, we charge it with electricity, and, having inserted it in the aperture, it touches the ball of the balance, which is immediately repelled: in moving away, this twists the thread by which it is suspended, and the amount of the twisting which is necessary in the opposite direction to bring it back again, and maintain it at a certain distance, measures the force of repulsion the balls then exercise. This measurement is effected by the glass or silken thread being attached, not to the tube, but to a stem carrying an index, which shows, on a graduated circle, the number of degrees through which the thread is twisted; and as the thread is exceedingly long in proportion to its thickness, and its elasticity almost exact, the force of torsion is taken as proportional to the angle through which the index moves.



By this instrument, into the detail of experiments with which it would be improper here to enter, Coulomb established the fundamental law of electrical attraction and repulsion; and it has been found, that from this law all the results of the distribution of electricity on bodies, its accumulation on and escape from points, that have been noticed, might be deduced.

The fundamental principles of electrical excitation, the distribution of electricity on bodies, and the manner in which the electric states of the excited bodies are related to each other, having been thus described, I shall pass to the explanation of the general principles under which those phenomena and laws have been arranged, and a knowledge of which we shall find necessary to our future progress. I shall lay aside all consideration of the more abstract theories of electricity, which refer it to mere molecular disturbance or to vibrations, and consider only those views which suppose the existence, in the one case, of two electric fluids, the theory of Dufay, and, on the other, that of a single fluid, the theory of Franklin.

Theory of two Fluids.—It is assumed that there exist in nature two kinds of electricity, each a highly elastic fluid, whose particles repel each other according to the law of the inverse square, while they attract the particles of matter, and also attract each other, according to the same law: that every body in nature contains usually an exactly equal quantity of each fluid; that bodies then are in their ordinary state; and hence, manifesting no unusual properties, we look upon them as being quiescent: but if a body contains more of one fluid than of another, it comes into an extraordinary state, and, acquiring new properties, we say that it has become excited.

Upon this view, the phenomena of electricity are capable of very simple explanation. When two bodies are rubbed together, the re-

sult is, that one electric fluid accumulates in excess upon the one, and the other upon the other body. They are thus both brought into a state of excitation; and as the excess of the one fluid must be exactly equal to that of the other, the excitation of both is equal, and, being opposite, must neutralize each other when they are brought to reunite. Of these electricities, that which passes to glass when it is rubbed with silk is termed, in the language of Dufay, vitreous electricity, and that which accumulates on resin when rubbed with flannel is called resinous. There are few bodies which may not assume vitreous or resinous excitation, according to the substance by which the friction is produced, and hence these names are liable to some objection, and are not much employed.

Since the electric fluids and matter attract each other, the bodies upon which the electricities become free appear to attract or repel each other according as they are invested by the same or opposite fluids, in consequence of the necessity of accompanying these fluids in their action on each other. Hence the electric attractions and repulsions which manifest themselves in all cases of excitation, and hence the bodies return to their indifferent condition as soon as the excess of electricity they contain is neutralized. It was for a long time supposed that the atmosphere, by its mechanical pressure, assisted in retaining the free electricities upon the surface of the excited bodies; but this is not the case. The air acts as an insulator of the excited body, without which no accumulation of free electricity could occur; but the mechanical pressure of the air may be removed without affecting the electrical conditions.

Theory of one Fluid.—In the hypothesis of Franklin there is assumed to exist but one electric fluid, of which, in its ordinary state, every substance contains a certain quantity. This fluid is considered to be highly elastic, to repel its own particles with a force varying as the inverse square of the distance, and to attract the particles of matter according to the same law. A substance with its proper share of electricity is therefore in its indifferent condition, possessing no properties beyond what we ordinarily attribute to it. But when two such bodies are rubbed together, a quantity of electricity abandons one and collects upon the other, and thus both are brought into an abnormal state, and assume the unusual properties which constitute excitation. The excitation is equal, for the one has gained precisely what the other lost; and by recombination they destroy each other's action, for they are brought to their original ordinary state. The excitation being produced, according to this view, by one body having electricity in excess, while that of the other is deficient, one is said to be *plus* and the other *minus* electrified; or, more generally, the one to be *positively*, the other *negatively* excited, and the signs + and — are often used as abbreviations for these words.

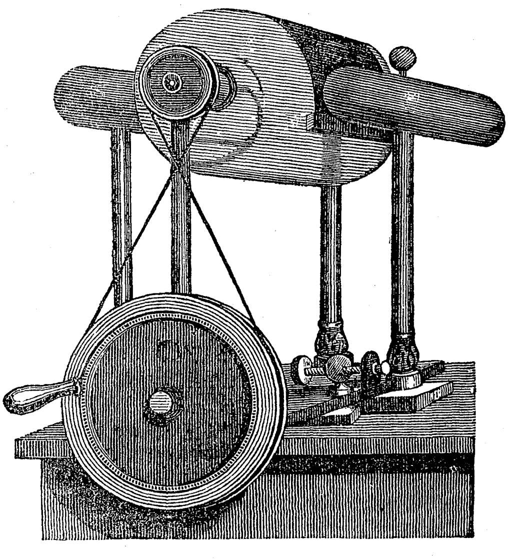
The particles of the electric fluid being mutually repulsive, and attracting those of matter, it is natural that two bodies having electricity in excess shall mutually repel, and that a body having an excess of electricity shall attract one having an excess of matter. Bodies both + therefore repel, a + and a — body attract each other. But, to explain the mutual repulsion of bodies both in the negative

condition, an assumption is required which at first sight appears to militate considerably against our reason; for as it is matter which is in excess in that condition, we must consider that the particles of matter mutually repel each other, according to precisely the same law, as it is demonstrated by the whole construction of the universe, that the particles of matter mutually attract each other. There is not, however, any real contradiction in these principles; the law of gravitation applies to matter in its ordinary state, in which it contains its natural quantity of electricity; and it affords no grounds for supposing that, if matter were deprived of that natural electricity, it would continue to attract. There is, consequently, nothing illegitimate in that assumption; and the theory of a single fluid may be as easily and successfully applied to the explanation of phenomena as that of the two fluids before described.

Already, indeed, considerable progress has been made towards a theory of electricity upon this idea. In order to account for the ordinary molecular constitution of matter, it is necessary to suppose that the forces which act upon its particles may change from attractive to repulsive, and again from repulsive to attractive, according as the distance between the particles is made to vary; and Mosotti has shown that it is only necessary to assume that the mutual repulsion of matter, when destitute of electricity, is inferior to its attraction for electricity, and to the mutual repulsion of the electricity itself, and the law of gravitation becomes a necessary consequence of the conditions under which alone electrical equilibrium can be established.

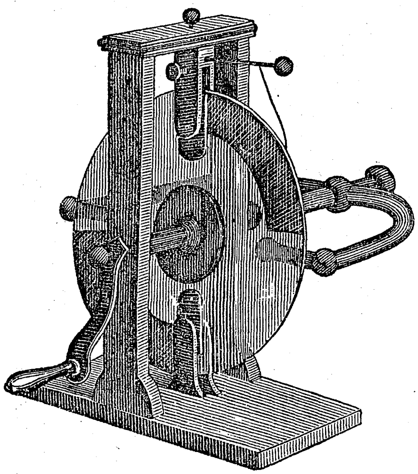
Such are the theories of electricity that have hitherto met with most general acceptation. In the succeeding portions of this work, I shall adopt the language of the theory of the two fluids, except that I shall use the words positive and negative fluids in place of vitreous and resinous; but I do so merely from convenience, and seek not to connect the idea of a fluid in any way more intimately with the true causes of the electrical properties of bodies.

Before passing to the description of the phenomena, and the discussion of the principles of electricity which yet remain, it is necessary to notice the construction of some electrical apparatus, which is employed in all cases where it is desirable to operate upon this agent in a state of high intensity and power. Of these the most important is the electrical machine.



The machine is in principle only a modification of the glass tube which, by friction with a piece of silk, evolved the electricity in the first experiments described. It consists of a glass having such a form as to expose a great extent of surface, and generally being used in the shape of a cyl-

inder, A, or of a plate. There are hence the cylinder and the plate machines. To produce the friction, an elastic rubber, B, is covered with silk, and made to press against the surface of the glass according as the plate or cylinder is turned round by means of the handle. The rubber being generally insulated, the electricity evolved upon it is at once collected, and may be transferred along conductors, or drawn as sparks from the knob of brass attached to it at the back. The electricity which is diffused upon the glass passes from its surface to that of a brass cylinder, termed the prime conductor, C, being collected by means of a series of pointed wires, which graze the surface of the cylinder according as it is turned round. The prime conductor is also insulated; and in the case of a cylinder machine, the glass itself is often supported upon insulating pillars, by which the loss of electricity is prevented. To increase the energy of the machine, the silk of the rubber is generally smeared over with a mixture of grease and an amalgam of tin and zinc, and a silken apron extends from the rubber half over the cylinder or plate to conduct the electricity to the points, and prevent its being carried away by the air.



Although I shall have occasion, when we have examined the relative action of excited bodies and conductors somewhat better, to notice the true theory of the prime conductor, yet for the present it may be considered as simply, from its proximity, collecting the free electricity on its points from the surface of the glass cylinder or plate, and by thus accumulating it upon a confined surface, enabling the experimenter to apply it or carry it to other bodies at his pleasure. When the machine is worked, the two portions of electricity become developed, as in the rubbing of the tube and handkerchief, upon the silk and glass; and if all be insulated, they attract each other so intensely that they break through the intervening air, and recombine across the surface of the cylinder, or round the edges of the plate, presenting the appearance of a brilliant spark, and accompanied by a snapping noise and a peculiar phosphorescent odour. To prevent this recombination, which would, of course, render accumulation upon the prime conductor impossible, the rubber, when the machine is required for active work, is connected with the ground by a wire or chain, through which the electricity which forms upon the silk makes its escape; and as new quantities are then liberated at each moment, those passing from the glass to the prime conductor, by the projecting points with which it is always furnished, collect upon it, and, acquiring a high degree of tension, pass under the form of sparks to any conducting body which may be brought near.

By means of a machine of such construction, the opposing properties of the electricities of the bodies rubbed together may be simply and completely shown.

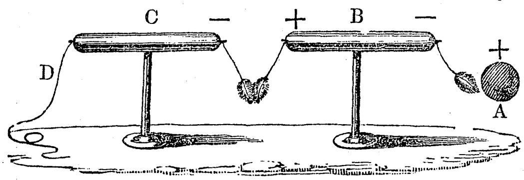
The degree of excitation of the prime conductor is generally, though not very accurately, shown by means of the quadrant electrometer. This consists of a stem of brass, which rests in a socket in the prime conductor, or, when not in use, in a wooden foot, as in the figure. To this is attached an ivory semicircular scale, of which a portion is graduated, from whence the name; on an axis at the centre of the ivory scale there is hung, by a light arm of whalebone, a pith ball, which, when the apparatus is unexcited, lies in contact with the brass stem, and thus assumes the same electrical condition with it when the instrument is placed on the prime conductor and the machine worked. The stem and the pith ball then repel each other, and the ball being consequently set in motion by the united repulsion, its radius moves through an angular space on the graduated scale, which serves in rough experiments as an index of the intensity of the excitation. Now if, when this instrument is fixed on the prime conductor, the latter be connected with the insulated rubber by a chain or wire, no matter how vigorously the machine may be worked, no signs of excitation can be produced; the electricity collected from the glass by the prime conductor passing along the chain or wire to unite with that which is developed on the rubber, and the two being evolved in equal quantities, complete neutralization is produced. That bodies similarly electrified repel each other, is shown by the principle of this instrument, as its indications of free electricity depend upon the stem and ball being both excited in the same way, and the repulsion being the same, whether it be fixed upon the rubber or the prime conductor.

To prove on a large scale, by means of the machine, that the opposite electricities attract each other, it is only necessary to place in connexion with the conductor on each side a metallic wire, tc which is hung, by a wetted thread, a ball of pith, or a cylinder of gilt paper. When the machine is turned, the balls attract each other across the cylinder, and touching, interchange the electricities by which they are excited, and thus the fluids, separated by the friction, are continually recomposed, being brought together by their mutual attractions. If to each wire there be hung two such balls, those of each side will be seen to repel each other, while they move towards those oppositely excited. Numerous experiments of an amusing kind, which it would be foreign to my purpose to introduce, are founded on these principles.

There have been now noticed four methods by which bodies may be electrically excited. 1st, by *friction*, which is, indeed, the only true direct excitation. 2d, by contact; as when an insulated brass disk excited by friction is touched to another, also insulated and neutral, a spark passes between them at the moment previous to actual contact, and the first is found to have divided its electricity with the second in proportion to its surface. In this case the two bodies, after contact, are in the same state of excitation. 3d, as where the prime conductor, which is neither itself rubbed, nor

does it touch the cylinder of the machine, yet *gathers* from it the electricity which is evolved thereon, and allows it to be transferred, under the form of the spark, to other bodies; and, finally, all the attractions and repulsions which have been observed indicate a power of action and excitation even at considerable distances; and this mode, which results from the attraction and repulsion of the electric fluids for each other, is, when examined, found really to comprehend the second and third modes of excitation, by contact and by gathering with points. There are, therefore, truly, only two means of excitation, this at a distance, which is termed *induction*, and that by *friction*.

It is not difficult to understand how bodies come to be excited by induction. Let us consider the insulated cylinders, B C, as being neutral, and having their natural electricities combined, and distributed uniformly over their surface. If a globe, A, excited, say with positive electricity, be brought near, it will attract the opposite electricity of B to the end which is nearest it, and repel the electricity of the same name to the farthest extremity; both electricities of B will thus become free, and B will be excited by the influence of the electricity of the body, A, at a distance; and the condition of B is characterized by its two extremities being in opposite states, and hence, at a certain point between them, perfect neutrality remaining. The positively excited end of B influencing C in a corresponding way, brings it also into an excited state, and this communication of action would go on through any number of bodies, the force set free being regulated by the law of the inverse square of the distance from the original disturbing cause at A. As long as A remains in its place, the state of electrical excitation is kept up; if A be totally removed, the natural electricities of each body recombine, and all become neutral; if A be brought very close to B, or B to C, the attractions between the opposite electricities become so great that they unite across the intervening space of air, and a spark passes. The bodies are then found to be in the same state, and the communication by contact, or the excitation which occurs, is shown to be only the termination of the inductive action. For suppose that A had 10 parts of + electricity, and that, by induction, it set free 5 of the — and 5 of the + fluid on the surface of the body B; then, when the spark had passed, the —5 destroying +5 of the body A, the two bodies should remain each with +5, and thus the results of contact described already should be produced.



The distance at which the combination of the electricities of the inducing and the induced body may occur, depends upon the intensity of the fluids collected on the parts of the surface nearest to each other; and hence, when there is on the body a point on which the great proportion of the liberated fluid, as has been already described, becomes accumulated, the fluid escapes from thence before

it is in sufficient mass to break its way under the form of a spark, and thus the permanent and similar excitation of the body silently occurs. This is the true theory of what has hitherto been described as the power of points to gather and to disperse the electric fluid. If a pointed body be excited by friction, it induces an opposite state in the particles of air by which it is surrounded, and communicates to them, with great rapidity, the charge which it had received. The prime conductor of the machine, being insulated, has its electricities separated by the inductive action of the excited glass cylinder or plate; the negative electricity collected on the points turned towards the glass escapes from thence, and unites with the positive fluid which had been set loose by friction, and proportional quantities of the positive fluid of the prime conductor being left free upon its surface, it serves the same purpose as a source of electricity as if it had come directly from the glass. A point placed on the prime conductor prevents the accumulation of the electricity, because it gives the + to the air as fast as the other points give the — to the glass; a point held near the prime conductor also prevents its excitation, by giving to it by induction — electricity as fast as it obtains + electricity from the glass of the machine.

In all these cases of induction where the electricities attract and repel each other, the bodies on which the electricities are collected will accompany them in their motions if they be not too heavy. Hence all the singular motions of bodies, when excited, are explained upon this principle. The variety of dancing figures, ringing bells, revolving wheels, affrighted heads, and so on, that are exhibited in popular lectures on this subject, will serve to practise the ingenuity of the student in tracing out their theory in the detail, with which it would be quite improper to occupy this work.

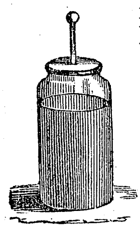
The theory of the Bennet's gold leaf electrometer, with which some of the most important principles of statical electricity are demonstrated, must not, however, be omitted. When an excited rod is brought over the electroscope, it separates the electricities of the metallic portions of the instrument, attracting the opposite to the upper surface of the cap, and repelling that of the same name into the gold leaves, which, being thus excited with the same electricity, repel each other, and hence diverge. If the exciting body be +, it is the + fluid by which the instrument appears affected; if it be —, the leaves diverge from the presence of — electricity. Hence if, when it is under the influence of a glass rod rubbed with silk, a stick of sealing-wax which had been rubbed with flannel be brought near, the divergence diminishes, until at last the leaves collapse completely, the resin having driven down as much negative electricity as there had been positive brought into action by the glass, and hence the gold leaves coming into their natural and indifferent condition. That it is by this inductive process that the gold leaves act, may be thus shown. If the cap of the electroscope be rubbed with a dry silk handkerchief, it becomes excited, and the leaves diverge with negative electricity; if then an excited glass rod be brought near, the divergence is neutralized, showing that positive electricity had been sent down by the glass; but if an excited resinous body be approached, the divergence increases, indicating the superaddition of electricity of the same name from the inducing power of the resin.

If, as in the figure (page 118), the cylinder C be connected with the ground by means of a wire or a wetted thread, D, the positive electricity passes from that body through the wire into the earth, where, from the enormous surface of the globe, it may be looked upon as lost, and the surface of C is altogether in a state of negative excitation. If, now, the exciting body A be taken away, the quantity of positive fluid returns along the wire, and brings the body C into its neutral state; but if before the body A be taken away, the conducting communication with the ground be cut off by

the removal of the wire or thread, the body C cannot get its positive electricity back, and hence remains in a state of negative excitation. In this manner a substance may, by induction, be made to receive a permanent charge. This is often useful in experiments with the electroscope, and the manipulation to charge it permanently is as follows: If it be desired to charge it positively, an excited stick of resin is held near, and the cap of the electroscope is touched with the finger. The negative electricity then escapes by the hand into the ground, and the positive electricity, accumulating over the cap and leaves, these last diverge. On then removing the finger, the leaves are insulated; and when the stick of resin is taken away, the permanent charge remains. To charge with negative electricity, an excited glass rod is to be used; and it will be recollected, that where the charge of the leaves is temporary, its electricity is the same as that of the exciting body; but where the charge is permanent, the electricity is of an opposite kind.

After the exciting body, in the latter instance, has been withdrawn, the divergence of the gold leaves becomes much greater than it had been before. This arises from the charge being increased by its action on the surrounding bodies, particularly on the glass by which the leaves are enclosed. By taking advantage of the increase of charge, by secondary inductive action, various forms of the electroscope have been contrived for rendering it more sensible, and are described in special treatises on electricity under the name of *Doublers* and *Condensers*. As they do not add anything to our knowledge of principles, and have no peculiar chemical relations, I shall not enter on their farther consideration.

One of the most interesting instruments in statical electricity, founded on the principle of induction, is the *Leyden Jar*, so called



from the city where its construction was discovered. It consists of a glass bottle, which is coated inside and outside, to a small distance from the top, with tin foil, and has fitted to the orifice a wooden or cork stopper, through which passes a stout wire, touching at the bottom the internal coating, and terminated outside by a metallic knob. When this jar is insulated, and the knob is touched to the prime conductor of the machine, and the handle turned, the positive electricity passes to the internal coating of the jar, and excites it to an equally powerful degree. This, then, reacting by induction upon the electricities of the external coating, separates them, attracting the negative to the side next the glass, repelling the positive to the outer side. The position becomes, therefore, + — +; and when the + fluid inside makes up by its greater quantity for the thickness of the glass by which it is separated from the — fluid, no more can enter into the jar. In this case the inside of the jar may be considered as being merely an extension of the prime conductor; and the electricities of the external coating, although separated from each other, are only in the quantities which had been always present. But if the external coating be connected with the ground, the + fluid, being repelled by that inside, passes away, and another quantity, entering from the prime conductor into the jar, decomposes a new quantity of the natural fluids of the external coating, of which also the positive escapes and the negative remains behind, held by the attraction across the glass to the positive fluid inside. New quantities of positive electricity entering continually from the machine, the accumulation of negative electricity on the outer coating proceeds, until the tendency of the two to combine is so intense as to break their way across the glass, cracking the jar, or to creep over the mouth from the edge of one coating to that of the other, and thus the jar discharges itself. To discharge a jar in which the elec-

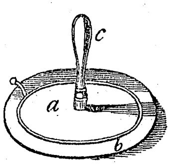
tricities are so accumulated, it is only necessary to connect by a wire the internal and external coatings; when the extremities of the wire, which are generally terminated by brass balls, approach, a large brilliant spark passes, accompanied by a loud report, and the jar returns to its original neutral state.

By thus collecting great quantities of electricity in large jars or in sets of jars (electrical batteries), the most beautiful and remarkable phenomena of electrical force may be exhibited.

The principle of the construction of the Leyden jar may be experimentally demonstrated as follows: First, it has been already explained that the jar, when insulated, is incapable of receiving any other charge from the machine than what its internal coating obtains by forming part of the surface of the prime conductor; the principle of induction requiring, in order that one electricity may accumulate upon its outer surface, the other shall be dissipated on the ground. Second, a light body placed between two balls, connected, one with the internal, and one with the external coating, is alternately attracted and repelled by each, and thus the accumulation on the two coatings is shown to be of opposite kinds. Third, the quantity of electricity which passes from the external coating may be shown to be equal to that which passes into the internal coating from the machine, by insulating the jar, and applying the knob of a second jar which is not insulated to its outer surface; this second jar will be found charged to the same degree as the first, and the inner and outer coatings will be respectively in the same state.

Statical electricity, thus accumulated in the Leyden jar, is capable of giving violent shocks to the animal frame, of evolving light and heat, and producing also powerful mechanical effects.

An instrument founded on the principle of induction, and which is of frequent use in chemical experiments, when an electric spark of moderate power is required, is the *electrophorus of Volta*. It consists of a flat cake of resin, *b*, which is generally spread on a circular board of eight or ten inches diameter. There is laid on this another circular plate, *a*, somewhat smaller, and which may be either of brass or tinned iron, with the edges turned up over a thick wire, so as to round it, or a board covered with tin foil. To this upper plate is attached an insulating handle of glass, *c*, and from its edge projects a wire terminated by a knob. The resinous plate, being warmed, is to be strongly excited by friction with a warm flannel cloth or a cat's skin, and then the upper plate is to be laid on it, and is touched with the finger. The negative electricity of this passes, then, into the ground, and the positive accumulates on the surface next the resin, of which



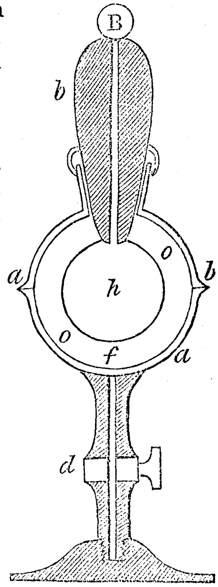
it, by induction, increases the negative charge. This new portion of negative fluid decomposes a new quantity of the electricities of the upper plate, which again reacts, and thus the plates are mutually brought into a state of very intense excitement. If, then, the finger be removed, the upper plate is insulated, and its charge of positive electricity retained upon it; and on applying the knob of the wire to any conductor or to the knuckle, a strong spark may be obtained from it; the instrument may be repeatedly charged and dischar-

ged in a few minutes, and retains its charge better than the electrifying machine.

This inductive action of electricity would at first appear to be exercised at a distance, altogether independent of the interposed substances, and to produce the motions to which it gives rise, as gravity causes the revolutions of the planets and their satellites, without the existence of any interposed medium; but a more exact examination shows that this is not the case. The substances inter posed in the path of the inductive action are necessary to its transmission, and modify, by their nature, its direction and amount; and it is, indeed, only from molecule to molecule of any substance, gaseous or solid, that the decomposition of the natural electricities can take place.

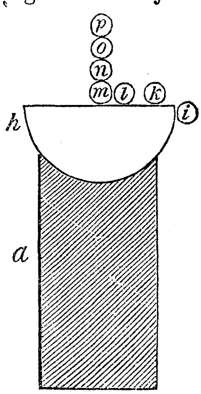
This may be beautifully shown by plunging in a vessel of oil of turpentine, which is an excellent fluid insulator, two brass balls, of which one is in connexion with the electrical machine, and the other with the ground. On turning the machine, the latter becomes excited by induction. If, now, a number of short shreds of sewing silk be mixed with the oil of turpentine, the mechanism of the inductive action is shown by each little bit of silk acting like the bodies B and C in the figure (p. 118); and attaching themselves mutually by their extremities, they transmit the electricity of the machine, by a series of decompositions, to the ball which is connected with the ground. If the excitation be very violent, the attractions and repulsions become too strong to be regularly transmitted; and this induction is accompanied by a powerful current of the particles of the oil from the first ball to the second. The particles immediately in contact with the directly excited ball acquire its state, and, being repelled, immediately pass off to that which has obtained, by induction, the opposite condition, and there become neutralized. Now what here occurs with the oil of turpentine takes place in ordinary induction with the air; every molecule of it interposed between the solid bodies becomes itself subjected to the inductive action, and forms a chain of alternate positive and negative poles, by which the effect may be transmitted to any distance. If the excitation be very great, the neutralization may occur with violence and rapidity, and generate currents, as in the oil of turpentine. It is these currents which, being produced by the repulsion of the particles of air from excited points, are rendered sensible in the effect termed the *electrical aura*, and are shown by the experiments of revolving flies. A still more violent and rapid recomposition of the electricities of the air molecules, which had been separated by induction, gives the electric spark in its various forms, such as the star, the brush, &c., according to the manner in which it is received and generated.

That the excitation by induction of a body at a distance is effected in this manner, from particle to particle of the interposed substance, is beautifully shown in the results obtained by Faraday concerning the influence of the nature of the medium on the amount of inductive charge transmitted. The instrument, which he has termed an *inductometer*, consists of a hollow sphere of brass, *a a b*, and a sphere of smaller size, *h*, also of brass, which is placed exact-



ly concentric with it. The interval between these, *o o*, may be occupied by any substance, as air, or glass, or sulphur; and then the central sphere being insulated from the outer by the shell-lac column *b*, and having been excited from the machine through the ball and wire B, the outer one is uninsulated, and the whole becomes a Leyden jar, in which the material may be varied at the will of the experimenter. By means of the tube and stopcock *f d*, the air in *o o* may be removed, and any other gas substituted for it. The outer sphere opens at *b* in two, so that melted sulphur or shell-lac may be poured in to form the inductive medium.

When the internal sphere is excited always to the same degree, the charge of the external coating should be the same, no matter what might be the nature of the intervening substance, if the action took place simply at a distance, after the manner of gravitation. But this is not the case. With the same internal charge, the excitation of the external sphere was found to be, that with air being 100, with shell-lac 150, with flint glass 176, and with sulphur 224. In these cases, therefore, the molecular excitation was transmitted in proportion to these numbers, which express, therefore, the degree of excitation that a common amount of inductive influence is able to produce in masses of these bodies. All gases, no matter how different in chemical properties and constitution, even though the temperature and pressure do not remain the same, possessed the same specific inductive capacity as air.



This principle is farther shown in an interesting manner by the fact that the induction is not exercised only in the straight line connecting the solid inducing and induced bodies, but that at every intervening point there is a lateral action exercised by the interposed molecules of air, which may be themselves considered centres of inductive force. Thus, if a cylinder, *a*, of shell-lac be excited by friction, and a brass hemisphere, *h*, placed on top of it, the intensity of the induced electricity will be found to depend not merely on the distance from the excited source and the nature of the interposed material, but to be more energetic in certain positions in the air, as when the carrier ball of Coulomb's torsion electrometer was placed at *o*, than when it was lower or higher at *n* or *p*.

Faraday has been led by his experiments to conclude that the difference between conducting and non-conducting bodies is, that the former assume with exceeding rapidity, under an inductive influence, this condition of molecular excitation, and hence appear to

allow the electricity to pass actually and instantly through their substance, whereas, in reality, it is only that the separation and recomposition of the electricities of the chain of molecules has been so accomplished. They lose also this condition as soon as the exciting cause has been removed, whereas non-conductors, when their particles have acquired electrical excitation, remain in that state of tension for a certain time. Thus, if the internal and external coatings of a Leyden jar were connected by a metallic wire, the inductive action would be propagated immediately across it; but the instant that the source of the excitation was removed, the electricities of the two coatings would recombine, from the facility with which the molecules of the wire can assume the inverse condition. But with an interposed plate of glass the result is different; the inductive action is propagated equally, but more slowly; and that it is the particles of the glass that really produce the charge by their excitation, is demonstrated by the fact that the metallic coatings may be removed, and yet the accumulated electricities be not disturbed; the tin foil serving only to discharge at the same moment every particle of the glass, as if a wire had been individually applied to each. That the induction has acted on the substance of the glass explains also the peculiarity of what is called the secondary or residual charge. When the particles at the surface have been discharged, they are acted on by the deeper molecules which are still excited, and hence acquire a second inductive charge; and with thick glass, and particularly with bodies which do not insulate quite so well as glass, there may be even a third or a fourth charge of this kind.

Conduction is therefore only the highest, most intense, and most rapid form of induction; and it appears from Faraday's investigations that the permanent excitation of an electrified body has its origin also in the inductive influence of the bodies that are around.

The source of the electricity evolved by the electrical machine cannot be considered as being positively known. Wollaston instituted a series of experiments, by which it appeared to be demonstrated that there was no electricity evolved except where chemical combination took place, and the superior power given to the machine by the amalgam of tin and zinc being spread upon the rubber was supposed to verify this idea. These experiments of Wollaston have been latterly repeated with great care by Peltier, and with different results; he found that the electricity evolved was proportional only to the amount of friction, and was the same under various circumstances of liability to the presence or absence of chemical action of the materials rubbed. It is therefore likely that, at least, the electricity of the machine may be generated by the simple molecular derangement and vibration which friction necessarily produces; and this view is very much supported by the undeniable fact, that by other agencies purely molecular, where no trace of chemical action can be pretended, the same form of statical electricity may be produced.

In almost all cases where the particles of bodies are suddenly and violently disarranged, the separated surfaces are found to be electrically excited; for instance, if a piece of mica be torn into thin leaves, these are powerfully electric. In many mineral substances a change of temperature causes a manifestation of electrical

polarity in a very remarkable degree; thus, if a long prism of tourmaline be heated, one extremity becomes positive and the other negative; when the temperature attains its highest point and becomes stationary, all symptoms of electricity disappear, but on cooling they return; in the inverse order, however, the end which had been positive becoming negative, and so on. In this case it appears as if the particles, in the internal motion which the expanding force of heat produces in them, acquired the same condition of polarity as they would have done by an external friction. If the expansive effect of heat and the consequent change of position among the particles of the tourmaline had been the same throughout, there would have been no reason for electrical disturbance; but this mineral, and some others which likewise become electric on being heated, as boracite, are exceptions to the general law of crystalline symmetry, and in other respects, as with regard to light, indicate a kind of structure which is very complex and peculiar. In such cases, an internal friction by the action of expansion on the unsymmetrically situated molecules of the crystal is the origin of the electrical excitation.

The source of statical electricity, which is of the greatest importance in nature from the universality of its action, is that of change of state of aggregation. When any body passes from the liquid to the solid, or from the liquid to the vaporous condition, or in the reverse order, from being solid or being gaseous becomes liquid, disturbance of the previous electrical equilibrium results. Thus, if a little melted sulphur be poured into a glass, or if melted tallow or resin be poured out on a metallic plate, the bodies after solidification will be found excited. If a cup of water be placed on the plate of the electroscope, and a red-hot ball of metal, or even a red-hot cinder, be dropped into it, the gold leaves immediately diverge by the influence of the negative excitement which is assumed by the water which remains, and which communicates itself to the metallic cup and to the instrument; if the gush of vapour had been allowed to impinge on the plate of another instrument, it would have shown excitation by positive electricity. This last is one of the most abundant sources of electricity; for as at all ordinary temperatures evaporation takes place from the surface of all the water of the globe, and the vapour produced, carrying with it the prodigious quantity of positive electricity which is thus set free, mixes with the air, our atmosphere is almost continually in an electrical condition, generally positive, but at some times, from interfering causes, negative. The great body of vapour, when condensed by the more elevated and colder regions of the air, collects into the peculiar condition which constitutes a mass of cloud, and therein is thus concentrated all the electricity evolved by evaporation at the surface. The clouds are, therefore, intensely electric; and when attracted by induction to each other, or to some prominent object on the earth, as a mountain-peak or an elevated building, the discharge and neutralization of the electricities take place with the brilliancy and destructive agency of the lightning, while the report, re-echoed from the surfaces of the remaining clouds, or by the sides of the adjacent mountains, produces the effect upon the ear of the continuous rattle of the thunder.

There is no doubt, however, but that in many cases of chemical combination and decomposition electricity in its statical form may be evolved; thus Pouillet proved decisively, that when charcoal is burned, the carbonic acid which passes off is in a state of positive excitement, and the residual mass of charcoal becomes negatively charged. When hydrogen burns in air, the vapour of water carries off the positive electricity, while the negative fluid distributes itself on the hydrogen remaining, and the vessel from which it issues. There is thus, in the combustion of our ordinary fuel, a vast source of the electricity of our atmosphere, in addition to that evolved by water in evaporating; and it has been found that the evaporation of a saline solution, as sea-water, produces a much greater degree of excitement than when the water is completely pure, owing, perhaps, to the destruction of the condition in which the salt and water had been united. The evolution of statical electricity occurs, also, when the chemical action is of a much more complex and obscure kind; thus, in the growth of a seedling plant, the carbonic acid which it evolves is in a positively excited state, and the substance in which the seed is imbedded becomes negative. It would appear, however, that frequently electricity that had been imagined to arise from the chemical relation of the bodies brought into contact, arose from their merely mechanical action on each other; thus the electricities produced by sifting lime and oxalic acid together on the plate of the electrometer are produced.

The mere contact of bodies has been supposed sufficient to evolve electricity upon

their surface. The trace of excitation in such experiments is so small, and diminishes so much in proportion as care is taken to avoid friction and other causes, that we may consider contact as being in itself without power.

The remarkable characteristic of statical electricity developed by any of these methods, is the amazing energy of its action on bad conductors, and on the best conductors if their substance be not of sufficient mass to give it free passage from one point to another; while it is only with difficulty that we can obtain, by means of it, the slightest chemical decomposition. In the language of the theory of electrical fluids, the electricity is developed in exceedingly small quantities by friction or change of aggregation, and hence can perform but feebly such offices as chemical decomposition, which depend on the quantity that passes in a given time; but this small quantity is gifted with immense tension; the few molecules which become polarized are so to an intense degree, and the attractive and repulsive forces which they exert are then sufficient to cause the greatest mechanical effects

SECTION II.

OF DYNAMICAL ELECTRICITY.

The sources from which electricity is derived in a continually circulating form, so that its properties shall result from its uninterrupted motion, must necessarily consist in arrangements from which all insulating substances are to be carefully excluded. In statical electricity, the connexion, by a conducting medium, of the opposite extremities of an inductively excited body, caused all electrical indications instantly to disappear, while that kind of connexion is absolutely necessary to the continuous flowing of the electricity which constitutes its dynamical condition; and when the conducting circle is broken by the intervention of the smallest portion of insulating matter, either all electrical excitation ceases, or at most a feeble trace of it remains, with the properties which characterize its statical condition.

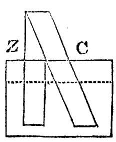
1st. Electricity thus circulating through conductors is found naturally existing in those substances which thereby possess magnetic properties. There is every reason to believe that the native loadstone, as well as all our artificial steel and iron magnets, are closed circles of dynamical electricity, set in motion by forces which depend on the chemical and mechanical constitution of these bodies. 2d. When any closed conducting circuit is at the same time unequal in mechanical constitution and in temperature, so that the current may pass more easily through one point than another, such a current is generated, flowing from the portion where the obstacle is greatest to that part where it is least. 3d. When substances capable of mutual chemical combination or decomposition act on one another, there is a current of electricity produced. In the case of simple union or double decomposition, the circle is internally closed, like that of a steel magnet; but where there is simple decomposition or replacement, the current may be directed through any kind of circuit; and thus constituting the most important branch of dynamical electricity, is called Galvanism or Voltaism, from the names of its most illustrious investigators.

4th. By means of organized structures, of which it is only lately, by the researches of Matteucci, that the true nature and functions have become known, certain fishes possess the power of transmitting a current of electricity across even imperfect conductors, and employ, instinctively, the effect of this current upon the living frame of smaller animals in order to obtain them for food. The

identity of the electricity from this animal origin, with the fluid of the other dynamic sources, has been completely proved, particularly by Faraday; and as the question of the anatomical structure of the electric organ, and of the peculiar part of the brain from which the electric nerves arise, interests the physiologist rather than the chemist, I shall merely state that the current so obtained possesses all the properties that will be described as characterizing galvanic electricity of very high tension, and allude no farther to it.

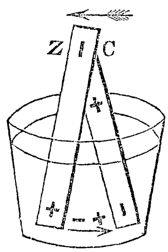
To the chemist, the electricity of the Galvanic or Voltaic battery is the most interesting of all the forms which this agent may assume, from the intimate relation which exists between it and the force by which the elements of bodies are bound together in chemical combination. To it, therefore, I shall especially direct attention, and consider the remaining sources only so far as the electricity which they yield may differ from it. I shall endeavour, also, to consider it only as characterizing bodies by their properties of exciting the current, or of conducting it when excited, deferring the important topic of the action of the current upon compound bodies until the nature of chemical affinities has been described.

Galvanic Electricity.—The manner in which this form of excitation occurs may be very simply shown. If a slip of perfectly pure zinc be partly immersed in a cup of dilute muriatic acid, this last remains totally without action on it, and there is no appearance of electrical disturbance; but if a slip of copper be introduced, which touches the zinc at C, out of the liquid, active decomposition of the muriatic acid begins, the chlorine combining with, and dissolving the metallic zinc, and the hydrogen making its appearance under the form of minute bubbles on the surface of the copper. At the same moment a remarkable state of electrical excitation is produced, in which the zinc resembles a body to which negative electricity, in a state of exceedingly low tension, is uninterruptedly supplied, while an equal quantity of the positive fluid flows along the copper, and these, uniting at the point of contact, produce the effects which are spoken of as those of the electric current, the passage of which may be rendered evident in a great variety of ways.



The precise manner in which the electrical excitement is here produced, may be explained sufficiently well without involving any consideration of the theory of chemical decomposition, which at the present moment would require a knowledge of principles that have not been as yet described. We may suppose, simply, that the chemical relations of the zinc and muriatic acid are such, that when placed in contact they mutually induce on each other a development of electricity: that part of the zinc which is immersed becoming +, and that out of the acid —, while the molecules of the acid near the zinc become —, and the general mass of the fluid obtains + excitation; the + electricity of the zinc being, however, balanced between the fluids of its own mass and of the acid, and the — fluid of the acid being in equilibrium between the + fluids of the zinc and of its own particles, it results that this condition of induced excitation may remain for any length of time without increasing or diminishing in intensity, the apparatus being in the condition of a very feebly charged Leyden jar: and on applying the slip of copper by which

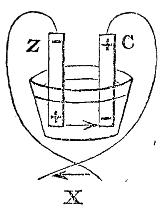
the excited surfaces, the zinc and acid, are placed in communication, the negative electricity of the zinc unites with the positive of the copper, whether by direct translation or by inductive action, and the positive electricity of the liquid unites with the negative of the copper to produce neutralization; at the same time the + of the zinc and the — of the acid combine. As, on the theory of Franklin, the



single electric fluid is supposed to pass from the body which is positively to the body which is negatively excited, it is usual to imagine this exchange of electricities to take place by a current, which in this case, as shown by the arrows in the figure, is from the copper to the zinc at the superior junction, but from the zinc to the copper in the acid underneath. At every moment, according as the neutralization of the electricities is effected, the system is competent to generate new quantities, and hence the analogy of the weakly-charged Leyden jar, noticed above, does not completely hold; for, to be accurate, it would require the jar to possess a power of charging itself as rapidly as it could be discharged

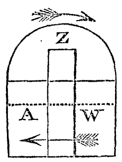
The passage of the current is accompanied by the solution of the zinc and the liberation of the hydrogen. This hydrogen accompanies the positively electrified molecules of the acid across the fluid, and is discharged under the form of gas upon the surface of the copper plate.

The essential elements of an arrangement by which a current of electricity may be produced are, therefore, first, two bodies, one simple and one compound, which act chemically upon one another in such a way as that the simple element shall be substituted for a constituent of the other, which shall be expelled; and, second, a conducting substance, which is indifferent in a chemical point of



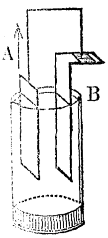
view, and only furnishes a route for the fluids of the actual elements to recombine continually with each other. In the example given just now, this conductor was a slip of copper; but it may be of any form, or almost any substance; thus, as in the figure, a wire may be soldered to the end of each slip, and on bringing these wires into contact at X, the current passes precisely as if the contact of Z with C had been direct. Such an arrangement is termed a *simple circle.*

It is not even necessary that the conductor should be solid or metallic; it is, indeed, only for convenience that the ordinary conducting plates and wires are metallic. Thus, in the figure,



A Z W, a plate of zinc is in contact on the one side with muriatic acid, A, and on the other with water, W, to which a better conducting power has been given by dissolving in it a little common salt. The current is then established, being from the conductor to the zinc, and from the zinc to the acid, precisely as in the former instances.

The passage of the current under these various circumstances may be shown, and also that, for its origin and transfer, metallic communication between the plates Z and C is not necessary, by a very simple experiment. If the slip of zinc be bent, as in B, and



a bit of paper moistened with iodide of potassium be laid upon it, and the wire from A be then brought to touch the upper surface of the moistened paper, the current passes in the direction of the arrow, and iodine is evolved at the point of contact of the wire. If the surface of the paper next the zinc plate, B, be examined, it will be found to be alkaline, from free potash. Thus the chemical action of the current, which will hereafter assume so important a position, may here be simply used as a test of its having passed.

The direction of the current depends upon the nature of the chemical action which is produced at the period of its passage, and on this principle is founded one of the most cogent and reasonable arguments in favour of the idea that the current is produced by the chemical decomposition, and not by the contact of the metals, as has been maintained. Thus, if a slip of iron and a plate of copper be immersed in muriatic acid, the action is altogether on the iron, and the current passes from the copper to the iron at the point of contact. But if the metals be immersed in a strong solution of ammonia, which acts upon the copper, but not upon the iron, the current is produced in the reverse direction. If persulphuret of lime, dissolved in water, be used as the exciting fluid with iron and copper, the current is from the copper to the iron through the fluid; but on using zinc and copper with the same fluid, the direction of the current is reversed; in the first case the copper, and in the last the zinc, is acted on: with acid solutions the copper would have escaped action, and the current would be in both cases from the iron or zinc to it, through the liquid.

It thus appears that the relation between the current and the chemical action is of the most intimate nature possible; the one, as Faraday and others have decisively shown, cannot exist in such arrangements without the other, and the nature and tendencies of one determine the power and the direction of the other; for the quantity of electricity which is set in motion in such an arrangement depends strictly on the amount of chemical decomposition which occurs in the liquid element, and is simply proportional to it.

It is usual to arrange the various bodies in a list with relation to a fluid, in which, if they be immersed and brought to touch outside, a current is generated from that of the two metals which stands highest in the scale to that which is below; the current through the fluid is, of course, in the opposite direction. The metals arrange themselves, however, very differently with different fluids, according to their liability to chemical action from them, as may be seen in the following table:

Dilute Nitric Acid.	Strong Nitric Acid.	Muriatic Acid.	Solution of Caustic Potash.	Yellow Hydrosulphuret of Potassium.
Platinum.	Platinum.	Platinum.	Platinum.	Platinum.
Silver.	Nickel.	Antimony.	Silver.	Iron.
Copper.	Silver.	Silver.	Nickel.	Nickel.
Antimony.	Antimony.	Nickel.	Copper.	Bismuth.
Bismuth.	Copper.	Bismuth.	Iron.	Antimony.
Nickel.	Bismuth.	Copper.	Bismuth.	Lead.
Iron.	Iron.	Iron.	Lead.	Silver.
Tin.	Tin.	Lead.	Antimony.	Tin.
Lead.	Lead.	Tin.	Cadmium.	Cadmium.
Cadmium.	Zinc.	Cadmium.	Tin.	Copper.
Zinc.	Cadmium.	Zinc.	Zinc.	Zinc.

At the head of each column is placed the name of the exciting fluid; on taking any two of the metals of the list beneath, and making them the solid elements of the circle, the current is, at the point of contact, from the upper to the lower, and is more powerful in proportion as the metals are farther separated from one another in the list; thus, with dilute nitric acid and with solution of caustic potash, the most powerful current is, after platinum, by silver and zinc; with muriatic acid by antimony and zinc, and with persulphuret of potassium with iron and zinc.

If the metals in contact with the exciting liquid be such as that one is totally without chemical action on it, it serves only as a means of mechanically transmitting the inductive force, and the current is simply due and is proportional to the electricity evolved by the action of the acid on the other. But if both metals be such that either would act upon the acid if by itself, and thus produce excitation, as when zinc and copper are placed in dilute nitric acid, then the molecules of acid are submitted to two polarizing forces in opposite directions, which, if equal, would exactly neutralize; but in practice they are not equal, and a current is produced proportional to their difference. Hence, the more nearly the metals resemble each other in their chemical relations to a given liquid, the weaker is the current they produce; but, though acting similarly to one liquid, they may be oppositely related to another, with which, therefore, they become a source of powerful excitation. Thus copper and zinc, being both acted on violently by sulphuret of potassium, generate but a feeble current, while with dilute acids, which act very differently on each, the current is very powerful; and thus platinum, which is inattackable by almost all liquids, forms the best possible element in every instance.

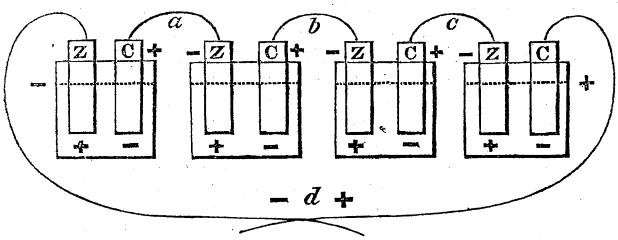
The metal which is used as the conducting medium conducts by having its natural polarity inverted; and hence, in place of a disposition to combine with the oxygen or chlorine of the liquid, it would, if already combined, abandon it; hence this metal remains clean and bright. On this principle was founded the mode of protecting the copper sheathing of ships, by attaching small portions of iron of about $\frac{1}{300}$ of the surface; the chlorine of the salt in the sea-water being thus transferred to the iron, and the copper, in place of becoming covered with the green rust of oxychloride of copper, remaining completely bright. This process succeeded in practice somewhat too well; for the negative elements of the sea-water being transferred to the iron, the positive bases present, lime and magnesia, were deposited upon the copper, and thus affording points of adhesion for marine plants and shell-fish, caused the bottoms of the vessels to become so foul as materially to injure their sailing powers. The process at present so extensively employed, of fixing a layer of zinc upon iron surfaces, acts in protecting them from rust in the same manner.

This transfer of the elements of the exciting liquids has become recently, in the hands of Spencer, the basis of one of the most beautiful and important of the applications of science to the arts. If one of the exciting liquids be a solution of sulphate of copper, as in Daniell's battery (page 136), the metallic copper which separates is deposited upon the surface of the plate to which the current passes in the liquid, and there is formed a layer of metal, which may be obtained, by slow and long-continued action, as dense and homogeneous as the best hammered copper. Any prominences or depressions, even a scratch of a pin, drawn on the plate on which the deposite forms, are accurately represented on its internal surface: and it is only necessary to use as the negative metallic element a medal in relievo or intaglio, to reproduce, with an accuracy equalling the powers of the most finished hand or machine, the finest works of art. This principle has been shown by Mr. Spencer to be applicable to the copying of all varieties of designs, and may be looked upon as the most important means of facilitating the possession of works of art, and thus elevating public taste, that has been made since the discovery of the method of transferring engravings to any number of steel plates.

The electricity which is evolved by the chemical action of such simple circles is remarkably different in its characters from that form which has been described as its statical condition. Although present in much greater quantity than can be developed by friction with the most powerful machines, yet, from its state of continued recombination, it cannot acquire intensity; it hence can pass only through good conductors; pure water, which, from the facility with which it allows of the passage of machine electricity, proves the

great source of failure and uncertainty in our experiments, intercepts almost completely the current from a simple circle, and the wires which are used to effect communication may be touched with the fingers without any tendency to lateral shock becoming evident; and yet the disproportion in quantity between the fluid, which bursts through the strongest insulating bonds of our apparatus, or breaks from the clouds, devastating forests, as the lightning, and that which passes silently across the wires of the voltaic circle, is such as almost to surpass belief. By actual experiment, the immersion of two wires, one of platina and the other of zinc, each 0·06 inch in thickness, to a depth of five eighths of an inch, in dilute sulphuric acid for three seconds, gave as much electricity as could be generated by thirty turns of the most powerful machine of the Royal Institution. Indeed, Faraday has shown that, in the current which passes during the decomposition of a grain of water, there is contained more electricity than in the brightest flash of lightning.

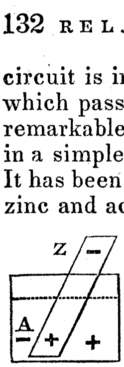
If the metallic elements of a simple circle be connected, not directly by metallic contact or by a wire, but by means of one or more other similar simple circles, interposed in the course of the current of its electricity, it is not at all interfered with, but the quantity of electricity which circulates is precisely equal to what is generated by the chemical action which takes place in each cell. For, considering the circle of four cells, represented in the figure, consisting of



copper and zinc plates, acted upon by muriatic acid, the copper of each cell discharges its positive electricity upon the negative fluid of the zinc in the adjoining cell, and hence there is neutralization of effect at the points *a*, *b*, and *c*, and it is only the amount of electricity liberated upon the copper and zinc plates in the terminal cells that passes along the wires, and, recombining at *d*, produces the phenomenon of the current; but this is the same quantity as should be evolved by any one of these simple cells by itself, and hence the remarkable result, which has been fully demonstrated by experiment, that no matter how we may increase the number of the elements of a galvanic circle, the quantity of electricity passing in the current is equal only to that evolved by a single cell. If the chemical action be not of the same energy in all the cells, there passes little more electricity than what is generated where the decomposition is least active; for, as the excess would have to penetrate through the liquid conductor in all the cells, the obstacle afforded to its progress is so great that it is almost totally absorbed.

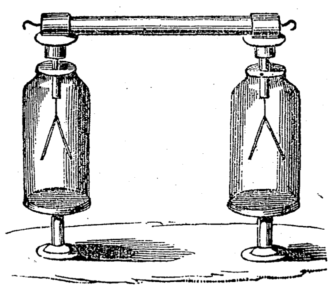
Although the increase in number of the elements of the galvanic

circuit is inefficient towards augmenting the quantity of electricity which passes, yet it changes the character of the current in a very remarkable degree, and confers upon the fluid an intensity which, in a simple circle no matter of what magnitude, it never can possess. It has been seen, that by the state of mutual excitation into which the zinc and acid are thrown before the circuit is completed, the inten-



sity of the evolved fluids is limited to that which will not suffice to enable the excited particles of acid to discharge themselves upon the oppositely excited particles of zinc; for if this discharge occurred, all should be brought back to the neutral condition. Now, if there be interposed a second cell, containing an equal quantity of the same liquid as the first, its particles must be brought into an equally excited state before discharge can occur; and as the electricity has then to pass through a bad conductor of double the length, it will require much greater intensity to penetrate it. The process, in virtue of which, therefore, the electric equilibrium is in the first instance disturbed, continues, even before contact is made, until the intensity accumulated is sufficient to propel the current across the interposed retarding liquid, and is hence proportional to the number of cells, or, as it is usually stated, to the number of pairs of plates. The peculiar character of intensity may be supposed to arise, also, from the electricity generated by the outside plates obtaining additional velocity, in passing across the intermediate cells, in each of which it meets an equal quantity of fluid moving in the same direction, and whose motion it absorbs, restoring them to rest, and being thereby hurried itself onward in proportion.

The intensity of the electricity which is thus excited is very slight, even where the number of combinations is considerable; thus, it requires a series of at least 200 pairs of plates, four inches square, immersed in dilute sulphuric acid, to cause a sensible divergence of the gold leaves of the most delicate electroscope. It is only where the arrangement involves some thousands of couples that electricity is evolved of sufficient tension to produce a spark across a non-conductor, such as that given by the electrical machine, or to cause any of those attractive and repulsive motions by which the feeblest form of statical electricity is recognised; to obtain these effects also, the circuit must be broken, for even with the most powerful combinations the current of electricity is without any action of intensity. Where, however, by means of a sufficient number of elements, intensity has been given, the quantity of electricity which accumulates, and the quantity of chemical action from which it has its origin, are exceedingly minute. This is exemplified in the dry piles of Zamboni, the form in which electricity may be considered as connecting its purely dynamical and properly statical conditions. The pile of Zamboni contains no apparent liquid element; it consists of disks of gilt paper, and of exceedingly thin zinc foil, laid alternately over one another, to the number of from five to twenty thousand,



care being taken to turn all the gilt surfaces the same way. These are enclosed in a glass tube, and terminated at each end by a brass cap with a pressure screw. The paper containing in its pores, when not artificially dried, a small quantity of water, this gradually acts upon the zinc, and electricity is evolved, which from the great obstacle presented to its recombination through the disks internally, and by the atmospheric air outside, attains a degree of intensity so high that it acts decidedly upon the electroscope, as shown in the figure, and is amusingly applied to produce various attractive and repulsive motions, such as ringing

bells, &c.; for there being a continual source of electricity in the action of the moisture of the paper on the zinc, these phenomena may continue manifested for years without diminution.

Such a dry pile, when insulated, shows opposite electrical excitation at the two extremities, these being, however, of equal force, and hence producing neutrality when combined. If, therefore, the two ends of a dry pile be connected by a wire, the electricities which had accumulated recombine, and the pile becomes inert, and requires a certain time before it can recover a charge equal to that which it had lost. When the pile is examined at a distance from its ends, the excitation is found to be less powerful, until at the centre it is exactly neutral. This arises from the action at each point being the resultant of the opposing actions of the two extremities, and vanishing at the centre where these last are equal, precisely as there exists a neutral place upon the surface of any body inductively excited by ordinary electricity. If the pile be held in the hand by one extremity, the electricity of that end is dissipated, and the other end becomes capable of acting more powerfully upon the electroscope, from the opposing influence being removed.

No principle has ever been discovered in science more rich in consequences than this of the increase of tension given to electricity in motion by the connexion of a number of simple galvanic circles. Hence, deservedly, the instrument so formed has obtained the name of the Voltaic pile. It has enriched chemistry with a crowd of important substances discovered by its means, and has led, by its results, to the suggestion of the most plausible theory of chemical combination that has been as yet proposed. In physical science it became the origin of all subsequent improvement in the domain of electricity, for without its agency it is hard to see how the steps which followed could have been made.

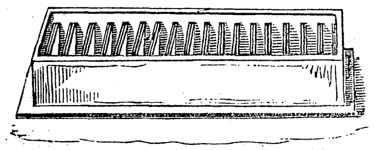
The form in which the Voltaic pile was first constructed was similar to that of the dry pile noticed above. The disks were of zinc and silver or copper. The fluid conductor, which was rendered more capable of acting on the zinc by the addition to it of some acid or of common salt, was imbibed in disks of common cloth, which were interposed between every pair of metallic disks. There were thus, copper-zinc, acid, copper-zinc, acid, copper-zinc, and so on to an indefinite extent. It is a peculiarity of this instrument, which, as it extends to many forms of it even now in use, and affects our chemical nomenclature remarkably, it is necessary to notice, that the current in the connecting wires appears to be in a direction opposite to that described in the battery of cells of page 131; for the outer copper plate at the one end, and the outer zinc plate at the other, having no communication with the exciting acid, transmit the current merely as portions of the attached wires, and hence the direction of the current is in appearance from the zinc to the copper end, while it is properly the copper from which the positive fluid emanates, and it is the negative which arises from the zinc. This diversity had its origin in the circumstance that the theory of the pile maintained by Volta, and even at the present moment supported by some illustrious men, ascribed the origin of the electricity not to the action of the acid upon the zinc, but to the contact of the zinc with the copper; the point where the metals touched being supposed to be a continual source of positive electricity to the copper. It was even attempted to prove this by soldering together plates of zinc and copper, and testing their electrical condition by the gold-leaf condenser, which was supposed to indicate a permanent state of excitation, independent of all fluid or chemically acting media. It has been fully proved, however, that, according as such contact experiments are made with increased care, the results become less evident in favour of that theory. Such trials tend to show the evolution of minute traces of statical electricity, where-

as the simple galvanic circle is characterized by the great quantity of electricity it may yield, and by its total want of statical intensity. Even, therefore, if it were proved, which it is not, that the mere contact of bodies evolved electricity affecting the gold-leaf electroscope, it would be as far from accounting for the totally different kind of electrical excitement by which the galvanic battery is created, as it would be from giving a true or satisfactory theory of the cause of magnetism.

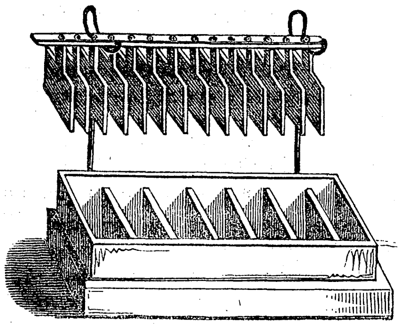
But the pretended excitation by contact, or the electromotor force, as it was termed by Volta, must be carefully distinguished from the capability of inductive excitement, which bodies capable of chemical action, as a slip of zinc and muriatic acid, mutually confer upon each other.

This last arises from the possible substitution of the zinc for the hydrogen of the acid, which does occur as soon as the interchange of the electricities allows of the transfer of elements; for on the first immersion of the zinc, the equilibrium of the chlorine and hydrogen, which had previously been totally engaged with each other, is interrupted, and that of the particles of the zinc, which had before been all circumstanced alike, is disturbed by some of them being nearer the acting muriatic acid than the others, and thus the induced condition of both arises. On this positive and necessary principle, the theory of the simple and compound circles already described has been given; and although it will require to be again noticed in describing the phenomena of decomposition which accompany the passage of the current, yet, for the only purpose which we here require, of studying the manner in which the current of electricity of the battery has its rise, the peculiar and important influence exercised by the chemical reaction among the elements of which it consists has been sufficiently described.

It is now necessary to notice more in detail the construction of some of the more usual forms of the Voltaic or Galvanic battery.



The first improvement on the pile of Volta consisted in placing it horizontally in a wooden trough, and replacing by cells containing dilute acid the moistened disks of cloth employed by the original inventor. It being difficult to cleanse the surfaces of the plates, which in that form were permanently cemented into the trough, this was made of delftware divided into cells, and the plates, being soldered together by projecting bands at the top, were hung upon a rod, as in the figure, so that, when wanted, they may be immersed with great rapidity, and withdrawn as easily from the liquid when the battery is not wanted. The power of such troughs is in-



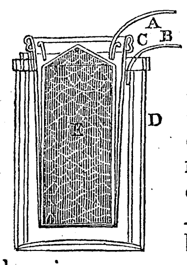
creased by one half when the copper slip is doubled over so as to oppose both surfaces of the zinc. Batteries intended rather for intensity than for quantity, and which consequently consist of a great number of plates of moderate dimensions, are generally employed on this last construction: each delftware trough holding ten pairs of plates, and any number of troughs that may be required being rapidly and easily arranged together. When a current of electricity of great quantity, but not of intensity, is required, it is usual to employ a few, or even only one pair of plates of considerable size. Thus, a sheet of copper and a sheet of zinc, each of from 80 to 120 square feet of surface, being kept separated by ropes of horsehair, have been rolled up together and immersed into a large tub of acid, forming thus a simple circle, giving a current so feeble in intensity as to pass with difficulty through a short column of distilled water, and to be quite insensible to the feeling, but which fused down into globules the most refractory metals, and gave with charcoal points a light of brilliancy insupportable to the eye. The copper plate may be very conveniently made to act as the cell containing the acid: cylindrical batteries of moderate size are very frequently so constructed.

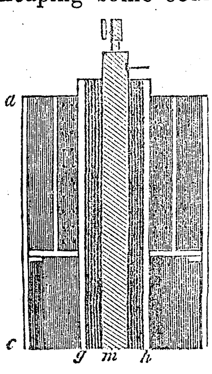
I have supposed, in the description of the nature of simple and compound Voltaic circles, that the zinc employed was completely pure, in which state, when first immersed in the acid, there is no chemical action, but only the preparatory inductive state produced, the decomposition of the acid by the zinc commencing only when the circuit is completed. But such pure zinc is too expensive for ordinary use, and the commercial zinc contains always traces of impurities, particularly iron, from which it acquires a power of generating a multitude of little secondary currents across the fluid, and thus preventing to a great extent the formation of the proper current. For suppose that there is on the centre of a plate of zinc a little piece of iron or of copper, this serves to return to the zinc from the acid the positive electricity, which had passed away from it precisely as if it had been a copper wire, which touched the acid with the one end, and the zinc plate with the other. Such a plate is therefore occupied almost solely with its own self-contained currents, and scarcely assists in generating the electricity which is brought into play in the battery at large. To this cause must be assigned the property which ordinary zinc possesses of dissolving readily in an acid, and of evolving hydrogen upon its own surface. It evolves the hydrogen upon those points of its surface on which foreign metals being deposited, serve to complete its circuits. This injurious property of ordinary zinc is remedied by coating the surface of the plate with mercury, or, as it is termed, amalgamating it. By this means the whole surface of the metal is brought into the same state, and must hence act in the same manner on the acid. Any secondary current which might arise could therefore find no means of discharge, and such zinc is not acted on until the circuit is completed, and then all hydrogen is carried by the excited molecules of acid to the copper plate, and there evolved as gas.

To amalgamate the zinc plates of a battery, a quantity of mercury is to be laid in a flat dish, sufficient to cover the bottom; moderately dilute nitric acid, to which a small quantity of nitrate of mercury

has been added, is to be then poured on the mercury, so deep that the zinc plate, when floating on the mercury, shall be covered by the acid. Before immersing the zinc plate, it should be, if not new, cleaned as well as possible with sand-paper from adhering dirt, and then it combines with the mercury very rapidly, so as to form a surface which, by rubbing with a little flannel, may be rendered completely uniform. The zinc should not be too highly mercurialized, for then it becomes extremely brittle, and requires considerable care in using it. The power of a battery may often be quadrupled by this method. A source of great inconvenience in the ordinary batteries arises from the hydrogen acting on the oxide of zinc which is dissolved, and reducing it to the metallic state, when it is carried, with the remaining hydrogen, to the copper plate, and deposited upon it. In this way there is gradually formed a second zinc surface opposite to the proper zinc plate, and which, tending to transmit a current in the reversed direction, neutralizes a certain proportion of the power of the circle, and may even destroy it altogether. Hence an ordinary battery is most active when first brought into play, and diminishes very rapidly in power until, after the lapse of some hours, even though the acid be not saturated, its action ceases.

This disadvantage has been beautifully removed by the principle of absorbing the hydrogen by means of a solution of sulphate of copper, which it decomposes, and precipitates upon the surface of the copper plate a layer of clean, new, metallic copper, in the best possible condition for supporting the action of the battery. The simplest arrangement of this kind is that of Mullins; the mechanical construction is most perfect in Daniell's constant battery. Mullins' battery consists of a delftware trough, D, in which the cylindrical zinc plate B, of nearly the same diameter, is placed, and inside of which, again, is the copper cylinder A, which is close, and acts only by its external surface; round the upper edge of the copper cylinder C is tied a bladder, into which fluid may be introduced by means of a row of apertures in the rim to which the bladder is attached. A solution of sulphate of copper is poured into the bladder, and its state of concentration is kept up by heaping some coarsely-pounded crystals on the top of the copper cylinder. Into the trough in contact with the zinc is then poured dilute sulphuric acid. When the action commences, the hydrogen is transferred through the membrane, and, meeting there the solution of sulphate of copper, is absorbed in the production of metallic copper. The copper cylinder never wears nor dirties. The metal is all recovered from the sulphate of copper, and the only thing necessary is that the plates of zinc shall be renewed from time to time. Daniell's battery has the advantage that the copper is outside, and hence is capable, with exposure of the same surface of zinc, of producing a much more powerful current. The cell con-





sists of a copper cylinder, *a*, *c*, near the top of which is attached a perforated plate, P, on which, when the cell has been filled with the solution of sulphate of copper, a quantity of crystals are laid, to be dissolved according as they are required. A solid zinc rod, *m*, supported at the top of the copper cylinder by a wooden cross-piece, is contained in a membranous bag, formed of the gullet of an ox, *g*, *h*, and into this is poured the dilute acid, which consists of one part of oil of vitriol and eight parts of water. Any number of these cells may be arranged together so as to give a battery, which, if all the coppers be connected upon the one hand, and all the zinc rods upon the other, will evolve large quantities of electricity of low tension; but when the copper and zinc elements are alternately connected with each other, the tension of the electricity evolved is much increased, though at the expense of the quantity generated.

The great advantage of such batteries is the perfect uniformity of their action, by which they deserve fully the name applied by Daniell to his construction, of the constant battery; with such an instrument, the conditions of the current may remain for days perfectly unaltered; and thus the laws of action of the current have been determined, particularly in its chemical relations, with complete success, and views of the analogies between affinity and electricity, equally novel and important, which will be discussed in another place, have been arrived at by its means.

Latterly, the membranous bags, originally used by Daniell and others as the diaphragm between the acid solution and that of the sulphate of copper, have been with great advantage replaced by porous cells of biscuit-ware, such as is represented in the figure by *g*, *h*.

Some forms of battery have recently been proposed, in which, under a small compass, very great power is obtained, by, 1st, bringing the plates very near each other; 2d, selecting solid elements, which differ as much as possible in their chemical relations; and, 3d, using as the exciting fluids those of the most intense action, and of the highest conducting power. In this way, the most powerful Voltaic combination that has been yet made is that of Mr. Groves. Plates of zinc and platina are separated by diaphragms of porous earthenware, the zinc being acted upon by dilute sulphuric acid mixed with some nitric acid, and the platina being in contact with tolerably strong nitric acid. The hydrogen evolved by the zinc is completely absorbed by the nitric acid on which it acts, forming nitrous acid which remains dissolved; and the metals, being those most opposite in their electrical relations, give the most powerful current possible.

The conducting powers of various bodies for this form of electricity has been determined with great care by Pouillet, whose results are, that the relative conducting powers of the various metals are expressed by the following numbers:

Palladium	5791	Brass from	900
Silver	5152	to	200
Gold	3975	Cast steel from	800
Copper	3838	to	500
Platina	855	Iron	600
Bismuth	384	Mercury	100

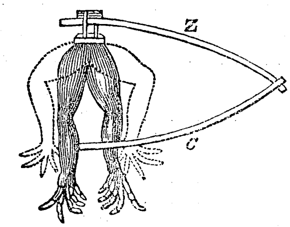
He ascertained, also, the relative conducting powers of the saline solutions usually contained in the cells of the Galvanic battery; and it appears that the conducting power of platina is two million and a half times that of a saturated solution of sulphate of copper, and hence that of copper is sixteen million times as great. The conducting power of the saturated solution of the sulphate of copper being taken as 10·000, he found that of

a saturated solution of sulphate of zinc to be .	4·170
distilled water	0·025
distilled water with $\frac{1}{20000}$ of nitric acid . .	0·150

The great retardation which occurs when the current has to pass through any considerable length of liquid, will now be easily understood. Pure water may be considered, with feeble circles, as an absolute non-conductor; and even with the most powerful combinations that have been yet made, the current is unable to force its way through the smallest measurable interval of air. It was not long ago believed that, even with simple circles, a spark indicating the passage of a current was seen on making contact, and hence that the electricity had passed before the metals had touched, and, consequently, that the chemical action should be alone considered as the source of the electricity. It is, however, now acknowledged, that no spark can pass until the wires have touched and are again separated, and the passage of the electricity is then accomplished, not by the action of the excited molecules of air, as occurs with the machine, but by the violent inductive polarization of the particles of the terminal conductors, which are torn off and pass from one pole to the other.

When the current of electricity is retarded by means of an insufficient conducting medium, the centre of the conductor becomes hot, and thus the most brilliant effects of heat and light may be produced; even the most refractory metals, as gold and platina, being, when in thin foil or wire, dissipated actually in smoke. By terminal points of well-burned charcoal, this phenomenon is beautifully produced, the ignition being totally independent of combustion, for it takes place in vacuo or in carbonic acid gas; and when the points are separated from one another to a certain distance, the interval becomes occupied by a splendid arch of light, formed by the inductively excited particles of charcoal, which, in a state of intense ignition, abandon the positive to attach themselves to the negative extremity of the conductor.

The action of galvanic electricity upon the animal frame does not properly fall within the scope of the present work, but in terminating the subject, the mode in which the first view of this important science was obtained may with propriety be noticed. Galvani was professor of anatomy at Bologna, and, while preparing frogs for some physiological experiments, he happened to touch, by one extremity of a metallic wire, the lumbar nerves which still remained attached to the spine, while

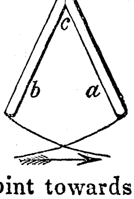


the other extremity of the wire was in contact with the muscles of the leg; these last were instantly thrown into strong convulsions. To perform this experiment with success, the legs of the frog are to be left attached to the spine by the crural nerves alone, and then a copper wire and a zinc wire being either twisted or soldered together at one end, the nerves are to be touched with one wire, while the other is to be applied to the muscles of the leg.

Galvani erred in the explanation of this remarkable effect; he looked upon the body as being in the state of a charged Leyden jar, of which the nerves and muscles were the external and internal coatings, and that, on connecting these by the conducting wire, the electricities recombined, and the passage renewed for the instant the phenomena of life. Volta pointed out, however, that, in order to produce full effect, the presence of two metals in the conductor was required, and he ascribed the origin of the electricity not to the body, but to the contact of the two metals, and supposed the convulsive motions to be merely the indication of the passage of the current across the body of the frog. This view has also been since modified by ascribing the electricity to minute traces of chemical action on the wires; but it was so fruitful in results, of which the construction of the Voltaic pile is the most remarkable, that Volta is, with justice, looked upon as the true originator of this branch of electricity as a science, although it was Galvani who observed the first fact belonging to it.

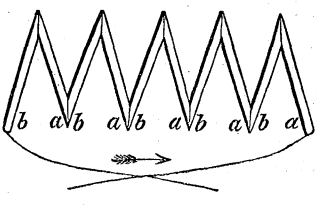
The frog so prepared is a most delicate test of the passage of a Galvanic current; it is truly a *galvanoscope*, corresponding to the gold-leaf electroscope for ordinary electricity; but it does not measure the quantity or intensity of the electricity which passes. As yet we have no exact measure of the intensity of Galvanic electricity; but that its quantity may be exactly determined, two of its properties may be applied: the first consists in determining the quantity of a given chemical substance, as water, which the current can decompose in a certain time, for the quantity decomposed is proportional to the quantity of electricity which passes; the second consists in observing the degree to which the current is able to deflect the magnetic needle from its natural position of north and south, for the angle of deflection is connected with the quantity of electricity in the current by a very simple law; we are not yet in a position to understand fully the theory either of the chemical or the magnetic galvanometer, and hence I merely indicate, for the present, their existence and their names.

Thermo-electricity.—If heat be applied to a wire, uniform in texture and thickness, bent into a ring, there is no disturbance of electrical equilibrium; but if any obstacle to the transmission of the heat, such as a knot or a coil in the wire, exist, a current will be established, of which the direction will be from the point of the circuit to which the heat is applied towards the point where the retarding cause exists. If in place of merely causing an artificial obstacle on a uniform wire, two metals, *a b*, be selected, which differ in conducting power, and the point at which they touch one another, *c*, be kept at a different temperature from the rest, a current is also produced from the latter point towards



the metal which is the worst conductor. The more unlike the metals are in molecular constitution, and the greater the difference between their conducting powers, the more energetic is the current. The best combinations are therefore of a crystalline and a non-crystalline metal, or of two metals which crystallize in different systems. Bismuth and antimony, which are the worst conductors of the metals, are also among the most crystalline; and while bismuth crystallizes in cubes, the form of antimony is a rhombohedron; these metals, therefore, combine all the essential qualities for generating a current when unequally heated, and they are, consequently, the most powerful sources of thermo-electricity that have been found. The results obtained with other metals will be understood by writing them down in the following order, any two of them being capable of forming a current when their junctions are unequally heated, the current being from the metal highest to that which is lowest in the list, and the power of the current being greater in proportion to the distance between the metals in the following order: bismuth, platinum, lead, tin, copper or silver, zinc, iron, antimony. The molecular texture would appear from this list to have more influence on the production of the current than the mere difference of conducting power.

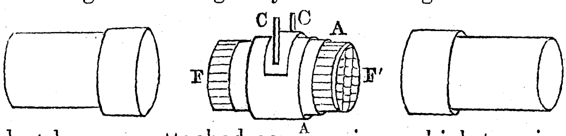
The intensity of the thermo-electric current so excited is exceedingly small; it is only capable of passing through very good conductors, and it requires the combination of a number of exciting couples to give sufficient tension to enable it to produce a spark, or to show any signs of chemical influence. It then, however, agrees in all respects with the electricity of the Galvanic battery when in an excessively feeble state of tension, and it resembles remarkably the hydro-electric current, in being able to reproduce at a distance the circumstances in which it originates; for precisely as a current passes through a combination of antimony and bismuth when its junctions are at unequal temperatures, so, when a similar current from any other source is passed through the metallic couple, a change of temperature is produced at the place where the two unite; if the current pass from the bismuth to the antimony, the junction becomes heated; but if the electricity pass in the opposite direction, the junction is cooled to a remarkable degree, so that, if a little hole be bored where the metals touch, and a drop of water be laid therein, it is frozen after a few moments. This result, which was first obtained by Peltier, and has been confirmed by Böttger, is one of the most remarkable proofs of connexion between the physical sources of temperature and electrical equilibrium that has been as yet discovered, and may influence our theories of the nature of heat in no inconsiderable degree.



The principle of strengthening the thermo-electric current, by combining together the action of a number of metallic couples, is due to Nobili. If we consider a number of bars of antimony and bismuth, *a b*, soldered together alternately at their ends, so that every alternate soldering shall be in the same plane, and the extremities of the terminal bars be

connected by a wire, on applying heat to the alternate solderings, a current is generated at each, which, being all in the same direction, travel together through the system, and thus increase its energy in proportion to the number of combinations. The important distinction between this and the combination of elements in the Voltaic pile is, that in the latter the increase of number affects only the tension of the current, but leaves the quantity the same as the single couple; but in the thermo-electric pile, although the intensity is increased, yet the quantity which passes in the current is augmented also.

It is this principle which has been applied by Nobili to the construction of the thermo-multiplier or thermo-electroscope used by Melloni and Forbes in their researches on radiant heat, of which a sketch has been given in the last chapter. The thermoscope consists of fifty small bars of bismuth and antimony, placed parallel beside one another, and forming a single prismatic bundle, F, F′, about $1\frac{1}{4}$ inch long and $\frac{3}{4}$ inch square in section. The two terminal faces are blackened. The bars of bismuth, which are arranged alternately with those of antimony, are soldered at their extremities, and separated all through their length by an insulating substance. To the



first and last bars are attached copper wires, which terminate in the pins C C, of the same metal, passing across a piece of ivory fixed on the ring A A. The space between the interior of this ring and the elements of the pile is filled by insulating material. The free extremities of the two wires are put in communication with the terminal wires of a magnetic galvanometer, the needle of which indicates by its motions when the temperature of the anterior surface of the thermo-electric pile is raised or lowered, in comparison to that of the posterior surface. (See P in figure, page 99.)

By means of a jointed support, the axis of the pile may be turned in any direction that may be wished; and to protect its surface from lateral radiation, the metallic tubes B B, brilliant externally and blackened on the inside, are attached to the extremities of the ring A A.

If by changing through one degree the temperature of a single soldering, a current of a certain power be obtained, there should be with fifty solderings a current fifty times as strong, or an equal current when the temperature of the solderings varies through one fiftieth of a degree. It has been ascertained that instruments of this kind may be made to indicate a variation of temperature of $\frac{1}{3000}$ of a degree on Fahrenheit's scale.

The electricity which is thus evolved by change of temperature in conducting bodies, although so feeble in quantity and intensity as to be utterly devoid of those brilliant qualities which attach much popularity to the phenomena of Galvanism and of machine electricity, has thus been found the means of assigning the true laws of some of the most interesting and important branches of the physical sciences; and it will be hereafter seen that thermo-electric currents,

excited in the superficial stratum of the globe by the inequality of temperature which arises from the action of the sun, may generate not only the magnetic properties on which are founded the commercial intercourse of civilized nations, but, by influencing the affinitary powers of the elementary constituents of our planet, may have been the agent in silently, but effectively, regulating the constitution of inorganic nature.

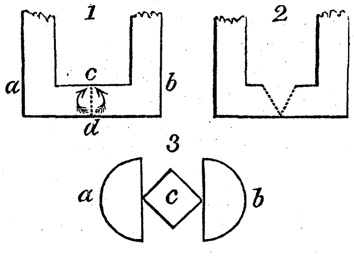
[From the extensive employment of thermo-electric currents as measures of temperature, it is desirable to understand their habitudes. Dr. Draper has shown that equal quantities of heat do not set in motion equal quantities of electricity; with certain combinations of metals the proportion increases, and with others decreases. For this reason, temperatures estimated in this way must always undergo correction, as the following table shows:

		Water boils.	Mercury boils.
	Mercurial thermometer .	212	662
Temperatures estimated by a pair of	Copper and iron . . .	202	257
	Silver and palladium .	235	880
	Iron and palladium . .	211	539
	Platina and copper . .	244	1030
	Iron and silver . . .	170	279
	Iron and platina . . .	212	829

We therefore infer, that in these six systems of metals, the developments of electricity do not increase proportionally with the temperatures, but in some with greater rapidity, and in others with less.

The tension of these currents undergoes a slight increase with increase of temperature: a phenomenon due to the increased resistance to conduction of metals when their temperature rises. In hydro-electric pairs, the quantity of electricity evolved depends on the surface of the plates; but in thermo-electric arrangements, the quantity of electricity is independent of the amount of heated surface, a mere point being just as efficacious as an indefinitely extended surface. And in a compound series of many pairs, the quantity of electricity evolved is directly proportional to the number of pairs.

Thermo-electric currents traverse metallic masses only on account of differences of temperature existing at different points. When a current flowing from the poles of a battery is made to traverse a wide metallic sheet, the whole of it does not pass in a straight line from one pole to the other, but diffuses itself through the metal, diverging from one pole and converging to the other. For these reasons, there are certain forms of construction which give thermo-electric arrangements peculiar advantages. For example, the surfaces united by soldering must not be too massive. Let *a*, fig. 1, be a bar of antimony, and *b* a bar of bismuth; let them be soldered together along the line *c d*, and at the point *d* let the temperature be raised, a current is immediately excited; but this does not pass round the bars *a b*, inasmuch as it finds a shorter and readier channel through the metals between *c* and *d*, circulating, therefore, as indicated by the arrows. Nor will the whole current pass round the bars until the temperature of the soldered surface has become uniform.

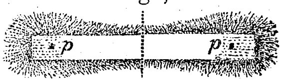


An obvious improvement on such a combination is shown in fig. 2, which consists of the former arrangement cut out along the dotted lines; here the whole current, as soon as it exists, is forced to pass along the bars. And because the mass of metal has been diminished along the line of junction, such a pair will change its temperature very quickly.

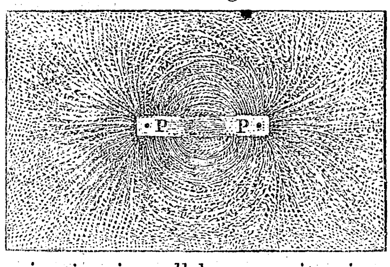
One of the very best forms for a thermo-electric couple is given in fig. 3, where *a* is a semi-cylindrical bar of antimony, *b* one of bismuth, united together by the opposite corners of a lozenge-shaped piece of copper, *c*. From its exposing so much surface, the copper becomes hot and cold with the greatest promptitude; and from its good conducting power, it may be made very thin without injury to the current.]

Magnetic Electricity.—The properties which are now known as magnetic were first recognised in a peculiar ore of iron, found in the vicinity of the town Magnesia, in Asia Minor, from which the names of the substance and of the science have been derived. The native magnetic ore or loadstone consists of iron and oxygen. This mineral, although quite inert with regard to all other bodies, attracts iron and steel with great power; and the pieces of iron and steel, while in contact with the loadstone, participate in its powers, and are capable of attracting other pieces to themselves. Iron and steel, though both attracted by the magnet, differ remarkably in the fact that iron, although magnetic while in contact with the loadstone, loses all its properties when it is removed; while steel, which is at first attracted with inferior power, when it has become magnetic by contact with that mineral, retains that condition after separation, and thus becomes a permanent artificial magnet. A steel magnet thus formed may in its turn be used in place of a loadstone to form others; and almost all the magnets we employ in experiments have thus obtained their power, as native loadstone is not found in sufficient quantity, or sufficiently intense in action, for our purposes. The steel bars which are magnetized are generally straight, but often also bent in the centre, so that the halves are nearly parallel, and are then called horseshoe magnets.

When a magnetic bar is dusted over with iron filings, it will be found that the filings attach themselves to the extremities of the bar, and scarcely at all to the centre; the magnetic power is thus seen to exist only near the ends of the bar.



Each filing being itself for the time a magnet, attracts others, so that they form strings, which arrange themselves, according to definite laws, in an order which is termed the magnetic curves, and from the disposition of these curves it is evident that the action of the magnet emanates from a single point, P, near each extremity; these points being the centres of action of the magnet, are termed its *poles*. Thus, in the figure, the bar being a magnet, the points P and P are the poles, and the directions of attractive force are indicated by the diverging lines, which, uniting on the inner side, form the magnetic curves.

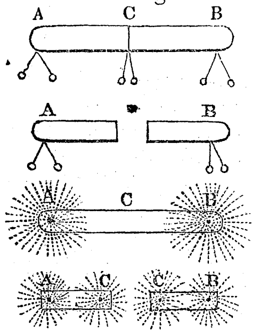


The utility of the magnet in navigation is well known; it arises from the poles of the magnet being attracted by the earth in such a way, that, when free to move, the magnet rests in a direction nearly north and south; the pole of the magnet which is turned to the north is termed the north pole, the other the south pole. If two magnets be brought into the neighbourhood of one another, they do not attract indifferently, as either would attract a mass of iron; but the north pole of one magnet attracts the south pole of the other, and is attracted by it, while the north poles of the two, or the south poles, if brought near each other, repel as powerfully. In magnets, therefore, poles of the same name repel, and poles of opposite names

attract, a condition precisely similar to that which holds between the electricities evolved by friction. In magnetism, also, the attractions and repulsions follow the law of the inverse square of the distance, and thus complete the superficial analogy which led astray for so many years the investigators of this branch of science.

The action of the earth upon magnets at its surface can only be explained by supposing the earth itself to possess magnetic properties. The northern portions of the earth attract the north pole of a magnet, and must therefore possess southern polarity; the southern portions of the earth attracting the south pole of the magnet, must possess northern polarity. The action of the earth cannot be explained, however, by supposing it to be a simple magnet with a pole at each extremity. It possesses at least two centres of force or poles in the north, one in Siberia and one in North America, while the exact distribution of the centres of magnetic force in the southern hemisphere has not been yet made out. These centres themselves are, however, not fixed; the needle is continually changing in direction; at present it points to 24½° west of north; but in the year 1664 it pointed to the north, and it had previously pointed in an easterly direction, towards which it is now returning.

Prior to the discovery, by Ampere, of the true nature of magnetic phenomena, a theory similar for the most part to that of the two electrical fluids was maintained; two magnetisms were supposed to exist, the particles of the same fluid repelling each other, but the particles of one fluid attracting those of the other. The assumption of magnetic properties by a piece of iron or steel in contact with a magnet became, therefore, a phenomenon of induction similar to that described under the head of statical electricity, the constitution of iron being such that the fluids recombined on the disturbing cause being removed; the constitution of steel, on the contrary, preventing their reunion. There existed, however, one great difference between a magnetic bar and a body excited by induction with machine electricity.



If the bar A, C, B, excited by induction, and of which the portion A is positive, and B negative, the middle C being neutral, be cut in two at C, the portions A and B retain their peculiar states, one positive and the other negative. But if the magnetic bar A, C, B be broken across at the neutral portion C′, then each half becomes a perfect magnet of half the strength of the entire; the points C′ and C″, which had been neutral, acquire magnetic power; and if these portions be again broken, each fragment is a perfect magnet. Magnetism belongs, in this way, to the inmost particles of the body, and in the general mass each magnetic molecule is still active and independent; a magnet resembles, therefore, an exceedingly bad conductor, which has been inductively excited by common electricity, and the particles of which retain for an indefinite length of time their state of polar excitation.

In order to understand the real nature of magnetic action, we must free ourselves, however, from all these analogies to machine electricity, no matter how well grounded they may appear to be when superficially examined. The electricity of the magnet is constantly circulating, and it possesses so little tension that it

never leaves the magnetic element, or molecule of iron or steel, in which it has its origin; in fact, every current of electricity possesses magnetic properties, and simulates the action of a magnet situated transversely to it. Thus, if a needle be held transversely on a wire carrying an electric current, it becomes magnetic precisely as if it had been laid parallel to a magnet; and by bending the wire round so as to form a coil, the magnetism which it confers being increased in proportion to the number of turns, may be rendered so intense as to surpass that of the most powerful steel magnets that are made. In fig. 1 a small coil is represented, by which magnetism is conferred upon the bar of steel inside. And in fig. 2, a large horseshoe of soft iron, by being covered by a helix of many hundred turns, may become able to raise a weight of some hundreds of pounds by the magnetism it acquires.

Fig. 1.

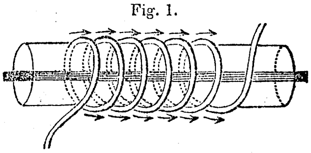
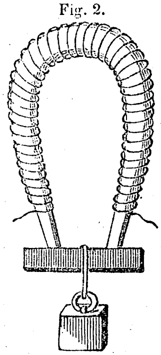


Fig. 2.



The coil of wire carrying the current may be shown, also, to possess magnetic properties by its attractive and repulsive action on a magnet. A coil as in fig. 3, suspended so as to be able to move freely, is attracted and repelled by the poles of a magnet precisely as if it also had a magnetic pole at each end. A flat coil, as in fig. 4, is also found to be magnetic, the pole's being indefinitely near each other at the centre of the coil. A beautiful form of the experiment consists in a long wire, which is made into a close coil, and connected at the ends with a pair of little plates of zinc and copper, as in fig. 5. On placing this system, buoyed by a piece of cork, in a dish of acidulated water, it settles itself at right angles to the direction of the magnetic needle, and behaves in all respects like a magnet situated in the centre of the coil, and perpendicular to its plane.

Fig. 3.

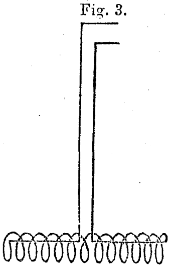


Fig. 4.

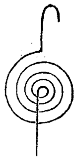
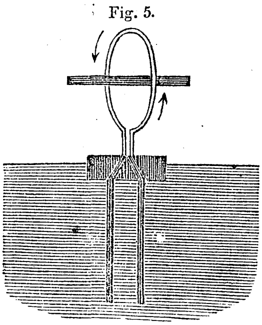
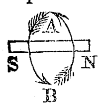


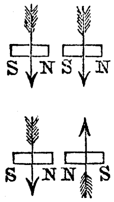
Fig. 5.



It is now necessary to examine into the relation which the direction of the current bears to the poles of the magnets which it forms, or which might represent its action. If A B be a wire in which a current is descending, as marked by the arrow, and a needle, N S, is placed transverse to it, the right-hand end of the needle becomes the north, and left-hand end of the needle the south pole; if the direction of the current be reversed, the north pole is formed at the left. In a circular current, the position of the pole may be, consequently, easily seen; the current A B, which descends in front

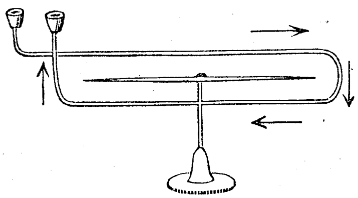


of, and ascends behind the needle, produces in the bar, N S, a northern polarity to the right, and a southern to the left; the action of magnetic currents upon each other supplies the explanation of these phenomena. If two wires carrying Galvanic currents be brought near each other, there is attraction or repulsion, according to the direction of the currents; if the two currents be in the same direction, the wires attract; if in opposite directions, the wires repel each other. The cause is evident on inspecting the figure: the upper wires being arrows which carry currents in the same direction, they act on each other, as should a pair of magnets placed transverse to their direction; the ends of the magnets which are juxtaposed have opposite polarities, and attract; while in the lower arrows, where the currents are in opposite directions, the effect is the same as would result from the magnets of which the contiguous poles are of the same name, and hence repulsion.



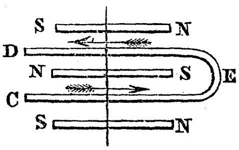
A wire carrying an electric current being thus a magnet, it acts upon permanent magnets, attracting or repelling, according to its position, and generally, from the combination of the two forces, generating very complex and singular motions. These actions have been so minutely and so extensively studied as to constitute a distinct branch of this department, termed *electro-magnetism;* but being unimportant in detail except in physical relations, I shall only notice the experiments by which Œrsted first created this branch of science, and which have ultimately led to one of the best measures of electricity, the multiplying galvanometer.

If a Galvanic current be passed over a magnet in the direction of the arrow in the figure, and the needle be movable on its centre, it endeavours to assume a position such as will bring it parallel, and with opposite poles presented to the magnet which the wire represents; and hence, in the figure, the motion would be to bring the south pole above the plane of the paper, and to depress the north pole below it, until the needle had assumed a position perpendicular to the conducting wire. If the current had been in the opposite direction, the action would have been reversed, and the north pole would have been turned up from the paper; but if the current be reversed at the same time that it is brought under the needle, as in the figure, it causes a deflection similar to that of the superior portion, and hence the angle through which the needle moves is much increased. If the needle were affected only by the current passing over or under it, its ultimate position would be, in all cases, at right angles to the current; but as the magnetic action of the earth tends constantly to bring it back to its direction of north and south, the position which it ultimately assumes is the resultant of the two forces.

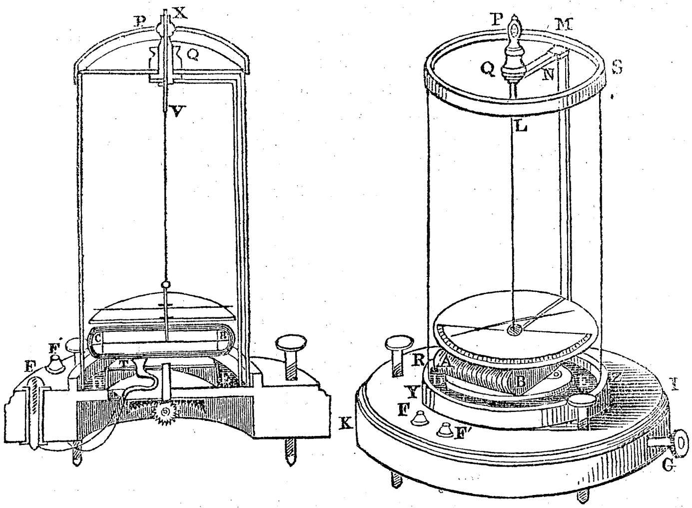


The deflection of the needle being thus an indication of the passage of an electric current through the wire, it is desirable in prac

tice to give the power of the current as much effect as possible, and at the same time to diminish as much as can be done the action of the terrestrial magnetism. The first is effected easily by increasing to the desired degree the number of turns which the wire makes round the needle; for the total effect, as will easily be understood from the description of the figure above, is proportional to the number of coils; but the diminution of the effect of the earth upon the needle requires some more care. If the needle be made but feebly magnetic, the power of the current to turn it diminishes just as much as the power of the earth to prevent its turning, and there is hence nothing gained; but the object is effected by using a combination of two, three, or four powerful needles, so arranged that with regard to the earth they are made to represent one very feeble needle. Thus, in the figure, the three magnets N and S, being suspended with their opposite poles next one another, act on each other so powerfully that the remote and weaker opposing action of the earth becomes almost insensible. A current passing in the direction of the arrows, C, E, D, will tend to depress the north poles of the upper and lower, and the south pole of the middle needle below the plane of the paper; and when it passes under the middle needle, its action upon it will be the same, since its direction is reversed. The amount of deflection of such a system of needles will still be regulated by residual terrestrial influence; but as this may be rendered as small as may be wished, the delicacy of the apparatus may be increased without limit. It is not desirable that the system of needles should be completely astatic, that is, indifferent to the earth, for then the degree of deflection by a given current would be affected by trivial and accidental causes; but by leaving a small residue of terrestrial magnetic effect, the current acts against this, and thus produces a deflection subject to an assignable law, by which the strength of the current may be determined. Within a certain limit, about 30°, the angle of deflection is proportional to the quantity of electricity flowing along the wire, but beyond that it follows a more complicated law, which, as involving mathematical relations, I shall not admit here. To obtain a greater degree of delicacy and uniformity of action, the system of needles is in all good instruments hung by a thread of glass or of silk, like the beam of Coulomb's balance (page 113). The deflecting force then acts against the force of torsion, and the resistance to be overcome is reduced to its simplest possible conditions.



The galvanometer, such as, with the thermo-pile, constitutes the thermo-multiplier, is represented in section and in perspective in the following figures; the same letters apply to both. A, B, C is the frame around which the copper wire is coiled, the ends T of which terminate in the metallic tubes F, F′. This frame is fixed on a horizontal plate D, E, which can turn in its own plane around its centre by means of a toothed wheel and endless screw, which are put in motion by the button G. Q, M, N is the support of the astatic system of two magnetic needles, suspended to a thread of cocoon silk V, L. R, S is the glass cylinder, secured by brass rings P, S,



Y, Z, which covers the apparatus, and rests on the base K, I. A graduated semicircle, accurately divided, is drawn upon the card, and by means of the supporting screws, and the movement of the frame A, B, C, the upper needle is brought to be exactly parallel to the coils, and to point to the commencement of the scale, being regulated in its height by means of the screw X, with which the silk thread is in connexion.

Where the current to be measured by the galvanometer is derived from a thermo-electric combination, it is necessary that the wire should be much thicker than for a similar current from a hydro-electric source, as the low intensity of the fluid thrown into motion by heat might cause false indications of its quantity, unless an ample path were opened through the best conductors for it; the number of coils for a thermo-electric galvanometer should also, for the same reason, be as few as possible. It is, therefore, not usual to employ the same instrument for these two kinds of researches. The position of the galvanometer in employing the thermo-electric pile in the researches on radiant heat, has been described, page 98, and its use in measuring the quantity of electricity flowing from galvanic sources, which has been already partly noticed, will be farther described in a future place.

The passage of an electric current in the vicinity of any substance capable of assuming magnetic properties is thus, by what has passed, shown to be sufficient for their excitation, and conversely if a magnet, whether permanent or temporarily produced, be brought near a substance through which an electric current may circulate, a current is immediately formed, the direction of which is always the same as that of a pre-existing current, which would have conferred on the magnet the properties which it actually has. In like manner, one current may generate another in a closed conductor near it, precisely as one magnet may produce another, or that a body statically excited may induce the electric condition on the

bodies in its neighbourhood; but such peculiar influences are too removed from the proper domain of chemistry to justify any detailed description of them.

In concluding this section of the subject of electricity, it is, however, important to prevent its being supposed that, by the omission of such considerations, they are to be considered as of inferior interest in the phenomena of nature. It is so much the reverse, that perhaps one of the most active sources of the electricity which we shall find to play a most important part in chemical combination, is derived from the induction of the magnetic influence of the earth itself: for the earth being rendered magnetic by means of the thermo-electric currents which circulate around it spirally from the equator to the poles, it is sufficient to bend a bit of copper wire into a ring, and whirl it round the finger in the plane of the magnetic equator, to obtain a current through the wire. A disk of copper revolving in this plane is a source of electricity derived from the inductive influence of the earth, differing, indeed, amazingly from the brilliant excitation of the thunder-cloud, but surpassing it far in real power of effect, and in the quantity of the electric fluid actually brought into play. We arrive here, indeed, at the extreme modification of this active and omnipresent force: we found it in the commencement, though existing in exceedingly small quantity, preservable only by the very best insulating means, and manifesting its tendency to escape by the attractions, the flashes, the mechanical violence which characterize machine electricity; while, in the form of magnetism, or of a magneto-electric current, though present in a quantity many millions of times greater, it flows uniformly, and almost insensibly, along the perfect conductors through which alone it is competent to pass, and it requires particular care to succeed in demonstrating its heating, its luminous, or its mechanical effects; but we recognise in it, nevertheless, the untiring agent by which the inorganic superstructure of the habitable globe has been produced, by which the depositories of the most important metals in the clefts of rocks have been accumulated, and which being thus the safeguard of navigation, the source of all metallurgic industry, becomes not less important to the civilization of mankind at large, than it is found, from its paramount influence on chemical affinity, its power to separate those elements most intimately joined, and to effect the union of those which appear most adverse to mutual combination, as well as the facility with which its principles may be applied to the explanation of the laws of chemical phenomena, to be available in the hands of the philosopher for the advancement of science.

To the chemist, therefore, the most useful property of electricity is the power which it possesses of modifying, annulling, or superseding chemical affinity. I have hitherto avoided as much as possible involving any ideas of chemical decomposition in the account of electricity just given, restricting myself to narrate such circumstances as might serve for the recognition of bodies by means of their electrical properties, independent of their chemical constitution. But the question whether electrical influence and affinity are identical, or what are their exact relations, and the discussion of the theory of electro-chemical combination, still remain, and will be examined when, first, the nature of affinity and the distinction between it and the action of cohesive force have been described, and the general system of nomenclature by which chemical substances are designated has been briefly noticed

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CHAPTER V.

OF CHEMICAL NOMENCLATURE.

THE general properties and laws of the physical agents, cohesion, light, heat, and electricity, having been now described so far as was necessary, that we may avail ourselves of those properties in characterizing the substances, elementary or compound, whose more peculiarly chemical relations we shall now proceed to study, it is ne-

cessary to prefix to the description of the forces by which chemical union is effected, and of the laws by which it is controlled, a short statement of the principles upon which the names of the substances to which there will be frequent occasion to refer have been constructed.

There are at present known fifty-five substances which the chemist has not been as yet able to separate into other elements. These are distinguished by the following names:

Oxygen,	O.	Potassium,	K.	Arsenic,	As.
Hydrogen,	H.	Sodium,	Na.	Antimony,	Sb.
Nitrogen,	N.	Lithium,	Li.	Tungsten,	W.
Carbon,	C.	Barium,	Ba.	Molybdenum,	Mo.
Boron,	B.	Strontium,	Sr.	Tantalum,	Ta.
Silicon,	Si.	Calcium,	Ca.	Chromium,	Cr.
Sulphur,	S.	Magnesium,	Mg.	Vanadium,	V.
Selenium,	Se.	Aluminum,	Al.	Uranium,	U.
Phosphorus,	P.	Glucinum,	G.	Gold,	Au.
Chlorine,	Cl.	Zirconium,	Zr.	Iridium,	Ir.
Iodine,	I.	Thorium,	Th.	Osmium,	Os.
Bromine,	Br.	Yttrium,	Y.	Platinum,	Pl.
Fluorine,	F.	Cerium,	Ce.	Tin,	Sn.
Tellurium,	Te.	Lanthanum,	Ln.	Lead,	Pb.
Mercury,	Hg.	Manganese,	Mn.	Bismuth,	Bi.
Zinc,	Zn.	Iron,	Fe.	Silver,	Ag.
Cadmium,	Cd.	Copper,	Cu.	Palladium,	Pd.
Cobalt,	Co.	Titanium,	Ti.	Rhodium,	R.
Nickel,	Ni.				

By the combination of these bodies among each other, the various substances which exist in nature are produced.

These simple bodies have been divided, from the earliest days of accurate chemistry, into two classes, the metallic and the non-metallic elements. The first thirteen in the list are non-metallic; the remaining bodies are metallic. It is found, however, that this division is only popularly correct; no matter how we may define a metal, we cannot avoid breaking through connexions of the most intimate and important kind if we endeavour to retain the class of metals as one founded on really existing chemical principles. Thus, in density and lustre, arsenic and tellurium are indubitably metals; and yet, if we class these bodies with copper or lead, we break through all laws of chemical analogy, for in their combinations they assimilate themselves most perfectly, one to sulphur, and the other to phosphorus. In selenium, also, the metallic characters are so feebly marked, that even did we not know that by its properties it must be classed with sulphur, we could not place it as a metal without great doubt.

In describing the simple bodies, I shall retain as a division the chemistry of the metals, for the classification, like all those which have been long in extensive use, has in some respects much utility and truth; but in cases where the study of certain bodies will be facilitated by departing from it, I shall not hesitate to do so. In order to avoid confusion subsequently, I shall here describe, as succinctly as possible, the nomenclature which has been adopted in chemistry; for in a science where the multiplicity of objects to be noticed is so great, it is of the highest importance that the principles upon

which the names of these objects are founded should be clearly understood.

In all conditions of science, the nomenclature has been regulated by the prevalent theoretical ideas of the time, and it is probably vain to look for a system of names which shall tell what the bodies really are, and not pretend to tell more; for that would suppose that we knew what the bodies are, whereas, in the most perfect state of science, we only know what we believe them to be. Thus, at a time when, by a mal-application to chemistry of the analogy of the human body and its soul, all bodies were looked upon as having a volatile and a fixed, an active and an inert element, the names of spirit of wine, spirit of hartshorn, and spirit of salt were invented; at a later period, when the theory of phlogiston prevailed in the minds of chemists, the spirit of salt became dephlogisticated marine acid; when the important functions of oxygen were pointed out by Lavoisier, the name was in his theory changed to oxymuriatic acid; and, finally, when the present view was introduced by Davy, the name hydrochloric acid became the most correct. The cause of this is, that in a good system of chemical nomenclature, we require two conditions which it is very difficult to successfully combine; that the name shall not only tell us that the substance is an independent substance, but that it shall give to us an idea of its most important chemical character, its composition; thus the name prussic acid is less strictly scientific than that of hydrocyanic acid, which shows us that its elements are hydrogen and cyanogen; and iron pyrites gives a less perfect picture of the body it describes than the words bisulphuret of iron. The necessity for indicating by the chemical name of a body its chemical composition, is thus what renders chemical nomenclature at once so variable and so complex, but it is also that which alone enables us to connect distinct ideas with our words.

The benefit conferred upon chemistry by the nomenclature introduced by Lavoisier and Guyton was scarcely inferior in its importance to the accurate ideas of combination in which it had its origin. The removal of the unconnected and unfounded names, which had been invented by the older chemists, and the invention of the idea that every name of a compound body should express its composition, involved the increase of accuracy in the minds of those chemists by whom science was subsequently to be prosecuted, which may be looked upon as the most fertile source of the discoveries made up to the present day.

The names most employed in chemistry are *acid*, *base*, and *salt.* The word *acid* signifying originally sour, was applied to all bodies which tasted like vinegar. The word *base* signifies any substance which, uniting with an acid, forms a compound, of which it is the basis or foundation; and the compound formed by their union, being generally similar to common salt in superficial characters, is termed a *salt.* Thus, oil of vitriol tasting, when mixed with water, sour, is an acid; soda is a base, and, when combined, they form the well-known salt called after Glauber, who discovered it. Such are the names of those classes of bodies, the discovery of which dates from a remote period.

Acting on the principle that, in naming a simple substance, the

name should be derived from its most characteristic property, Lavoisier formed the word "oxygen" from οξυς, acid, and γενναω, I generate, to signify the important substance, the functions of which he was the first to show, and which he imagined to have the peculiar property of forming acids. In like manner, he constructed the word "hydrogen" from υδωρ, water, and γενναω, to express its most important property, of being an element of water. This principle can, however, seldom be rigidly acted on; for example, oxygen is as much a *water former* as hydrogen; and the name of oxygen itself is not without objection, as the pre-eminence as acid former, which Lavoisier imagined it to possess, has been latterly overthrown. In the case of simple bodies, names derived from quite arbitrary sources, as tellurium from *tellus*, the earth; selenium from σηληνη, the moon; vanadium and thorium from Vanadis and Thor, deities of Scandinavian mythology; chlorine from χλωρος, yellowish green (its colour); and similarly iodine from ιοειδης (like a violet), have a great superiority over those which, by attempting to teach more when first invented, have the disadvantage of teaching falsely at a future period.

The simple bodies, combining with each other, form compound bodies of the first order, or *binary compounds*. The names of those binary compounds which contain oxygen are of two kinds, according as the compound possesses acid properties or not; if it be an acid, the word acid is added to that of the other body to which the termination *ic* is joined. Thus the acid compound of sulphur and oxygen is *sulphuric acid;* the acid compound of phosphorus and oxygen is *phosphoric acid.* It frequently happens that the same body forms with oxygen two acids, in which case, that containing most oxygen retains the terminal *ic*, while that in which there is least oxygen ends in *ous*. Thus there is *sulphurous acid*, and *phosphorous acid*, consisting of sulphur united with less oxygen than could form the sulphuric or the phosphoric acids. Many bodies form, however, with oxygen more than two acids, and in this case a new principle of nomenclature has been introduced: the words ὑπο, hypo, and ὑπερ, hyper, under and over, are prefixed to the degrees terminating as before stated. Thus there is an acid of sulphur containing less oxygen than the sulphurous acid, and it is called *hypo-sulphurous* acid; and also an acid containing more oxygen than the sulphurous, but less than the sulphuric acid: this might be called either *hyper-sulphurous* or *hypo-sulphuric acid;* the latter name has been universally adopted. Chlorine forms, with oxygen, four acids, which are the *hypo-chlorous acid*, *chlorous acid*, *chloric acid*, and *hyper-chloric acid*, or, as it is often called, substituting the shorter Latin *per* for the Greek ὑπερ, *perchloric acid.*

In cases where the compound formed with oxygen is not an acid, it is termed an *oxide* of the substance with which the oxygen is united. Thus oxide of lead, oxide of iron, oxide of copper, are respectively the compounds of oxygen with lead, with iron, and with copper. In many cases, where oxygen unites with bodies in more than one proportion, one compound may be an acid, and the other not. Thus manganese, uniting with oxygen, gives *manganic acid* and *permanganic acid*, but in a lower degree of oxidation it forms several

oxides of manganese. For as a substance uniting with oxygen may form many acids, so may it form many *oxides* also; and in such cases it becomes necessary to distinguish them from one another This is done by the adoption of the Greek words προτος, δευτερος, τριτος (first, second, third), prefixed to the word oxide. Thus we say protoxide of lead, deutoxide of lead, tritoxide of iron; the oxide which contains most oxygen is often called the *peroxide*, and that which contains least the *suboxide*, as *peroxide of manganese*, *suboxide of copper*. The word *sesqui* (one and a half) is also used for oxides intermediate between protoxides and deutoxides, but the nomenclature then involves numerical proportions, which will require to be described herafter.

Some other simple non-metallic bodies, in combining with the metals, form compounds, of which the names are constructed on the same plan as those of the metallic oxides. Thus,

Chlorine	forms	Chlorides.	Bromine	forms	Bromides.
Iodine	"	Iodides.	Fluorine	"	Fluorides.

The compounds of sulphur with the metals having been popularly named before Lavoisier's time, and it being desirable to retain, as much as possible, the names already in common use, a different form of termination is adopted for that body and some others. Thus,

Sulphur	gives	Sulphurets.	Nitrogen	gives	Nitrurets.
Selenium	"	Seleniurets.	Phosphorus	"	Phosphurets
Tellurium	"	Tellurets.	Arsenic	"	Arseniurets.
Carbon	"	Carburets.			

To distinguish between the different sulphurets or chlorides, &c., of the same metal, the Greek prefixes are adopted, as in the case of oxides. We have thus *proto-chloride* and *deuto-chloride* of manganese; also *perchlorides* and *subchlorides*. The Latin *bis* is often substituted for the Greek *deuto*, as the bichloride of tin in place of the deuto-chloride. Among Continental chemists, names which should be translated *chloruret* in place of *chloride*, and *sulphide* in place of *sulphuret*, are frequently employed; but as these are founded on certain theoretical ideas that have not yet been discussed, the propriety of adopting such additional terminations cannot be considered until we have proceeded farther.

Where two non-metallic bodies are united, it is a question how the name of the compound should be formed. Thus, in a compound of chlorine and phosphorus, should it be called chloride of phosphorus or phosphuret of chlorine? This is decided by referring to the classification of the simple bodies which will be hereafter given, and which is founded on a view of all their chemical properties taken together. Whichever element stands highest in the scale gives the characteristic name to the compound body. Thus chlorine is above phosphorus, and we say *chloride of phosphorus.* Iodine is also above phosphorus, and we say *iodide of phosphorus;* but iodine is below chlorine, and we hence call the compound which they form *chloride of iodine.*

The combination of the metals with each other, except in some

peculiar instances, are termed *alloys*. Thus we say brass is an *alloy* of copper and zinc; fusible metal is an *alloy* of bismuth, tin, and lead. Where one metal is mercury, the alloy is termed an *amalgam* of the other metal; thus, an *amalgam* of silver is an alloy of mercury and silver; an *amalgam* of tin is an alloy of mercury and tin. Arsenic and tellurium are so far removed from the metals by their chemical characters, that their compounds with the proper metals have the peculiar termination in *uret.*

By the union of two primary compounds there is formed a *secondary compound.* These secondary compounds are generally termed *salts.* The word *salt* is, however, applied to numerous classes of primary compounds. Thus, the metallic iodides, chlorides, bromides, and fluorides are recognised as salts. It is now also a debated question whether the bodies formed by the direct union of an acid and an oxide are really primary or secondary compounds; but I shall now describe only the ordinary nomenclature of those bodies, postponing the discussion of their intimate constitution to another place. When an acid and a metallic oxide, both primary compounds, combine to form a secondary compound or a salt, the specific name of the salt is that of the base, without any change; we thus say a *salt of soda*, a *salt of oxide of copper;* the generic name is taken from the acid, the word *acid* being omitted, and the final *ic* being changed into *ate*, or the final *ous* into *ite.* There is thus formed from sulphuric acid and soda *sulphate of soda.* From nitric acid and oxide of lead, *nitrate of oxide of lead.* From sulphurous acid and potash, *sulphite of potash.* From hypochlorous acid and lime, *hypochlorite of lime.* Where the salt contains an oxide of one of the common metals, it is usual to suppress the words *of oxide* in its name, and thus to say sulphate of copper in place of sulphate of oxide of copper; nitrate of lead in place of nitrate of oxide of lead. The strict correctness of language is thus sacrificed; but if the idea of the composition of the salt be held clearly in the mind, the abbreviation is not injurious; this mode of naming salts is so universal, that breaking in on it might be productive of more injury than allowing it to remain; I shall therefore say, for example, *nitrate of lead*, understanding, however, that the nitric acid is combined not with lead, but with oxide of lead.

It frequently happens that a metal forming with oxygen two oxides, will form with acids a class of salts for each oxide. In this case the words *proto*, *deuto*, *sesqui*, or *per*, by which the oxides are distinguished from each other, are prefixed to the generic name of the salt. We thus say proto-sulphate of iron, persulphate of iron; indicating that there is in one salt the protoxide, and in the other the peroxide of iron. We have sesqui-sulphate of manganese, and deuto-sulphate of platinum. The relative quantity of acid and base being liable to variation, there are acid salts with an excess of acid, and basic salts with an excess of base. In such case, the proportion of acid is marked by the Latin *bi*, *ter*, &c., as *bisulphate of potash*, and the proportion of base where it is in excess by the Greek δις, τρις, &c., as di-sulphate of zinc, tri-sulphate of mercury; or still better by the words bi-basic, tri-basic, &c., to indicate the quantity of base; there is thus tribasic-sulphate of mercury, quadribasic-sulphate of copper, and so on.

There are many other kinds of *secondary compounds* than the salts just noticed. Thus water enters into numerous compounds, which are called *hydrates*. This water may act in very many different capacities, and its nomenclature must be varied accordingly, as will be seen under its proper head; but where we wish to indicate that a body contains water, without determining more nearly the specific function of the water, we describe the body as being *hydrated*.

Oxides and *chlorides* combine together to form secondary compounds, which are called oxychlorides, as the *oxychlorides of mercury*, the *oxychloride of lead*. *Oxides* and *sulphurets* combining form *oxy sulphurets*, as *oxysulphuret of antimony*. *Chlorides* and *sulphurets* form by their union *chloro-sulphurets*, as *chloro-sulphuret of mercury*.

When two chlorides combine, the compound is termed *a double chloride*, or a *chloride* of the metals; as the *chloride of gold and sodium*, the *chloride of copper and potassium*. In the same way there are *double iodides* and *double bromides*. But where two sulphurets unite, the nomenclature has received an important change.

Berzelius has proved that, in very numerous cases, where a body forms an acid with oxygen, which acid uniting with a metallic oxide forms a salt, that body, uniting also with sulphur, gives a sulphur acid, which, uniting with a sulphuret of a basic metal (a sulphur base), forms what he terms a sulphur salt. Thus double sulphurets are salts, consisting of a sulphur acid united to a sulphur base Hence, as arsenic combining with oxygen forms arsenious acid, so, uniting with sulphur, it produces *sulpho-arsenious acid*, which, uniting with sulphuret of lead, forms *sulpharsenite* of lead, precisely as the oxygen acid, uniting with oxide of lead, produces what should be called *oxyarsenite of lead*. The prefix *oxy* is, however, not used; the ordinary salts are supposed to contain the oxygen acid, and it is only where a salt does not contain an oxygen acid that an additional word is necessary to point out what sort of acid it does contain. Tellurium and selenium act like sulphur; there are *tellurium acids* and *tellurium bases*, *selenium acids* and *selenium bases*, and hence, in place of calling the compound of seleniuret of antimony and seleniuret of sodium a double seleniuret, it is called the selenio-stibiate of sodium.

An attempt was made to assimilate the nomenclature of the chlorine and iodine bodies to that of the oxygen and sulphur compounds; thus, to call chloride of mercury a chlorine acid, and chloride of sodium a chlorine base, and the compound which they form a chlorine salt, *chlorohy drargyrate of sodium*. This idea, however, has not been received into science; for, indeed, now the direction of the ideas most popular among chemists points precisely contrary, and in place of assimilating the double chlorides to ordinary oxygen salts, there is a general tendency to class the ordinary salts along with the simple chlorides.

Ternary compounds are formed by the union of two secondary compounds. Thus *dry alum* is a compound of *sulphate of potash* and *sulphate of alumina*. Compounds of this order seldom exist in more than one proportion. Alum combining with water to produce the *crystallized alum*, generates a *quaternary compound;* and even more complicated stages may be attained; but they are so rare, and of so little scientific importance, that they do not require notice here.

In organic chemistry, the principles of nomenclature are for the most part identical with those now stated; where deviations occur, they will be noticed under their proper heads. The progress of sci

ence has, however, introduced remarkable changes in the mode of representing the constitution of bodies, particularly by means of the symbolical nomenclature now universally adopted after Berzelius.

In the list of the simple bodies in page 150, the name of each substance is accompanied by its symbol, which is generally the initial letter of its Latin name; and in cases where the name of more than one body begins with the same letter, they are distinguished by adding to the symbols of all the bodies but one a second letter in smaller type, which may be the second letter of the word, or whatever letter will best serve to characterize the name.

If there be but one non-metallic substance in the group, it is generally selected to be denoted by the single letter, as C. and P. for carbon and phosphorus, while the metals whose symbols have the same letter are denoted by Ca., Co., Cd., Ce., and Pl., Pb., Pd. Where there are more than one non-metallic body commencing with the same letter, it is a matter of indifference which is designated by the one or by the two, but the single letter is generally attached to the body which is of most importance in chemical phenomena. Thus S. is sulphur, while Si. and Se. denote silicon and selenium respectively.

The symbols of compound bodies are constructed by grouping together the symbols of their constituents; thus Pb.O. represents a compound of oxygen and lead; C.H.N.O. a compound of carbon, hydrogen, nitrogen, and oxygen. The algebraic sign of addition is frequently used to connect symbols, as Cl.+S., chloride of sulphur; I +K., iodide of potassium. But I shall use that sign only where I wish to express that the bodies so connected are united by an inferior degree of affinity; thus Cl.Ca. is chloride of calcium dry, but when crystallized it becomes Cl.Ca.+6H.O., in which the + sign is used to show that the water is united with the Ca. Cl. by a power distinct from, and inferior to, that which retains Ca. and Cl. in combination. Water thus combined is often represented by the symbol Aq., for water is capable of acting in a variety of ways in combination, and, as will be shown when we come to speak of the chemical relations of water, it requires to be expressed sometimes as H.O. and sometimes as Aq.

But that which requires special notice in speaking of symbolical nomenclature is, that it involves essentially the idea of numerical relations. Thus the symbols Pb. or Cu. do not call up to the mind of the chemist the simple ideas of lead or copper, but of a quantity of lead and of a quantity of copper, in the proportion of 103·6 and 31·7, which is termed an equivalent of each. Thus, also, the symbol Pb.O. signifies not merely a compound of lead and oxygen, but specially a compound of an equivalent of lead and an equivalent of oxygen, in the proportion by weight of 103·6 of lead and 8·0 of oxygen. It is thus that the symbol $Pb.O_2$, or Pb.+2O., which represents also a compound of lead with oxygen, shows to the chemist that this second body contains to the same 103·6 of lead twice as much, or 16·0 of oxygen, as had existed in the former. Pb.O. is therefore *protoxide*, and $Pb.O_2$ is the *peroxide of lead.*

The details of the application of those symbols involve thus the numerical laws of constitution, which have yet to be described; and

hence it is unnecessary to develop their arrangement farther at present. It was necessary to allude so far to them when speaking of nomenclature, as I may have occasion to introduce some of them in a general way in the next chapter.

CHAPTER VI.

OF CHEMICAL AFFINITY, AND ITS RELATIONS TO HEAT, TO LIGHT, AND TO COHESION.

The peculiar power by which we suppose chemical phenomena to be produced, is specially distinguished from cohesion, and from all other forces in nature, by exerting in the different kinds of elementary or compound substances various degrees of energy; and by its capability of acting upon certain bodies exclusively, and in preference to acting upon others, which, so far as physical circumstances go, appear equally exposed to its effects. Thus, if to some liquid muriatic acid there be added a mixture of lime and magnesia, the lime will all dissolve in the acid before any trace of the magnesia will be taken up. If a slip of iron be placed in a cup of nitric acid, a large quantity of deep red fumes is immediately expelled from the acid, with an appearance of boiling or effervescence; and the iron disappears, being taken up by the liquid in place of the substances which had been expelled. If a slip of copper be dipped in the acid, the same effect is produced; but if the iron and copper be left together in the acid, no action takes place upon the copper until the iron shall have been totally dissolved. The muriatic acid, therefore, presented equally to lime and magnesia, combines with the lime in preference, and the nitric acid takes up copper, giving off, to make room for it, a quantity of gaseous elements (nitrous acid fumes) it had previously contained; but it will take iron in preference to copper, if the two be presented to it at the same time. Chemical affinity is therefore *elective;* it chooses among a variety of bodies which it will act upon, and is thus different from cohesion or gravity, which will act upon all bodies equally exposed to their influence at the same time.

In the example of the metal and nitric acid, there is involved a second phenomenon, which, equally with elective affinity, is characteristic of chemical force. It is *decomposition.* The copper cannot dissolve in the nitric acid without the expulsion of another substance. By a simpler example, the decomposition may be rendered more evident. Sulphuret of hydrogen consists of sulphur and hydrogen; if it be brought into contact with iodine, the iodine expels the sulphur and takes the hydrogen; the sulphuret of hydrogen is *decomposed*, and a new body, iodide of hydrogen, is formed. Here the hydrogen chose between iodine and sulphur, and preferred the former: the greater affinity for the iodine caused the decomposition. Hydrogen has, however, a still more decided tendency to combine

with chlorine; and if chlorine be brought into contact with iodide of hydrogen, the iodine is in its turn expelled, and chloride of hydrogen formed. Here is a series of decompositions depending on the relative power of the affinities of chlorine, iodine, and sulphur for the one body, hydrogen. Thus, by the elective affinity of an uncombined body, choosing among a variety of other bodies all equally uncombined, there is produced a new combination, containing that for which its affinity was strongest. But when an uncombined body is put in contact with two substances already united, it tends to separate them, to combine with one and to set the other free.

If we could combine any one body, as hydrogen, for example, with every other of the simple substances, we might, by such experiments as those described with the sulphuret of hydrogen, iodine, and chlorine, obtain an idea of the exact order of intensity of the affinity of each of them for hydrogen, and could easily represent, under a tabular form, such an idea. This has accordingly been tried, and was, indeed, the result of the first sound ideas of the nature of chemical affinity which were obtained. It was not done completely in any case, for even at present our knowledge is not sufficient to enable us to form a series, including all the simple bodies. It was particularly in the chemistry of the salts that the benefit of this principle was found, and it was to explain and predict the result of the decomposition of salts that tables of the elective affinity were constructed.

It has been stated that, if lime and magnesia be placed together in contact with muriatic acid, the acid will dissolve all the lime before it acts upon the magnesia; the affinity of lime for muriatic acid is therefore greater than that of magnesia for the same acid, and hence, if to a solution of magnesia there be lime added, the magnesia will be expelled and the lime will take its place. If to the lime solution of soda be added, the lime will separate, and soda may be in turn expelled by potash. On the other hand, there are many metallic oxides which enjoy a still more feeble affinity than magnesia; thus, if to a solution containing oxide of iron, magnesia be added, the oxide of iron is thrown down and the magnesia taken in its place. In this manner may be arranged a series of compounds, consisting of different bases, in union with the same acid; and by observing the order of decomposition by each other, a view of the relative affinities which they exercise may be formed. If, also, a series of acids be combined with the same base, a similar view of their relative affinities may be drawn up. Thus, when a solution of potash is exposed to the air, it absorbs carbonic acid, for which, therefore, the potash has an affinity of a certain energy; on adding acetic acid, the carbonic acid is expelled, and acetate of potash formed; on adding nitric acid, the acetic acid is expelled from it, and nitrate of potash formed; and from this, by means of sulphuric acid, the nitric acid may be recovered, the potash remaining in the state of sulphate.

The results so described may be exhibited as follows, by writing in a column the names of the different acids, in the order of their affinities for a certain base (soda), which is placed at top. Similarly

in a column, at the top of which is placed the name of a given acid, the various bases in the order of their affinities may be written. Thus:

Soda.	*Muriatic Acid.*
Sulphuric acid.	Potash.
Nitric acid.	Soda.
Muriatic acid.	Lime.
Acetic acid.	Magnesia.
Carbonic acid.	Oxide of iron.

For the simple bodies similar lists might be constructed: thus, in the same way as the series of affinities for hydrogen already noticed, a table of affinites of the different metals for oxygen may be drawn up from observation. If to a solution of nitrate of silver, in which the silver is combined with oxygen, a globule of mercury be placed, it dissolves, and the silver is set free. By dipping into the solution of nitrate of mercury a slip of copper, the mercury is thrown down, and the copper takes its place. From the nitrate of copper the metal may be thrown down by lead, and the lead again precipitated by a plate of zinc. The affinities of the simple bodies for each other may be therefore expressed, taking hydrogen and oxygen as illustrations, by the following columns:

Hydrogen.	*Oxygen.*
Chlorine.	Zinc.
Iodine.	Lead.
Sulphur.	Copper.
	Mercury.
	Silver.

in which any one body in the list may expel all below it from combination, and will itself be expelled by every body below which it stands.

Such is *simple elective affinity;* but it often manifests itself in a more complex form, as when it acts among a greater number of bodies than three; and by the mutual action of two compound bodies, two new ones may be formed. Thus, when nitrate of lime is decomposed by potash, there is simple decomposition, and the lime is set free; but if, in place of pure potash, we employ carbonate of potash, the result is the formation of carbonate of lime; for when the potash leaves the carbonic acid to go to the nitric acid, and the nitric acid leaves the lime to go to the potash, the carbonic acid and the lime, finding themselves in presence of one another, unite, and precipitate as carbonate of lime. The nature of the decomposition may be more clearly shown from the figure:

$$\left\{\begin{array}{l}\text{Nitric acid.}\\ \text{Lime.}\end{array}\right. \quad \left.\begin{array}{l}\text{Potash.}\\ \text{Carbonic acid.}\end{array}\right\}$$

The bodies existing before mixture being composed of those written above one another, and those formed by decomposition consisting of those which are in the same horizontal line.

This action is termed *double decomposition.* In the example just stated, the difference between it and simple decomposition may

appear to have been accidental, the potash acting precisely as if it had been free, and the lime and carbonic acid uniting only because they came into contact, without any other ties, and hence combined together; but the peculiarity of double decomposition is, that by means of it, reactions may occur which could not have been produced by simple affinity, and which, on the contrary, appear to have been produced in opposition to it. Thus, ammonia cannot decompose nitrate of lime; on the contrary, lime will take nitric acid from ammonia; and yet, if we mix a solution of nitrate of lime and carbonate of ammonia, they decompose each other, and, by double elective affinity, there are formed nitrate of ammonia and carbonate of lime. As in the former diagram, the compounds, before and after mixture, are found arranged in the horizontal and vertical lines of the diagram:

$$\left\{\begin{array}{ll}\text{Nitric acid.} & \text{Ammonia.}\\ \text{Lime.} & \text{Carbonic acid.}\end{array}\right\}$$

In fact, in order to understand the cause of such double decomposition, we must take into account not merely the affinity of the ammonia for the nitric acid, but that of the lime for the carbonic acid. Thus, if the affinity of lime for nitric acid be represented by 80, and that of ammonia for nitric acid be represented by 70, the lime will be the stronger, and can, when by itself, expel ammonia; but if the carbonic acid intervene, and the affinity of lime for carbonic acid be 50, and of ammonia for the same acid be 30, then decomposition must occur; for the forces preventing decomposition are the affinities of nitric acid for lime, and of carbonic acid for ammonia; that is, $80+30=110$; while those tending to cause decomposition are the affinities of nitric acid for ammonia, and of carbonic acid for lime, $=70+50=120$; the latter are the more powerful, and the constituents of the two salts consequently exchange places. The former affinities are termed the *quiescent*, the latter the *divellent* affinities; and whenever the sum of the divellent is greater than that of the quiescent affinities, decomposition must occur.

Thus the simple affinity of hydrogen for sulphur is much greater than that of mercury for sulphur, and the affinity of mercury for chlorine is much greater than its affinity for sulphur; and yet, on bringing chloride of mercury into contact with sulphuret of hydrogen, complete decomposition ensues, chloride of hydrogen and sulphuret of mercury being produced. In this case, the affinity of mercury for chlorine being 20, and for sulphur being 10; the affinity of hydrogen being for sulphur 15, and for chlorine 30, the result may be shown as follows:

$$20\left\{\begin{array}{c}\overbrace{\text{Chlorine.}\qquad\text{Hydrogen.}}^{30}\\ \underbrace{\text{Mercury.}\qquad\text{Sulphur.}}_{10}\end{array}\right\}15$$

the force producing decomposition being $30+10=40$, and greater than those, $20+15=35$, which tend to keep the elements as they were.

Such are the results of chemical affinity manifesting itself in its simple and in its more complex form; hence there would appear to be nothing more easy than to determine the scale of affinities, and to construct a series of tables in which all existing substances

should find their place, and all possible cases of chemical decomposition might be foretold with the same accuracy as the law of gravitation allows the disturbing effects of a new planet to be calculated; but, unfortunately for the simplicity of expression which the laws of chemical affinity would thus assume, new and unexpected complications arise, and embarrass all our explanations; thus, if we take muriatic acid, and form a table of the affinities of bases for it, we shall find that it is as given in No. 1, and constructing for sulphuric acid an independent column, we shall find it to be as in No. 2.

No. 1.—*Muriatic Acid.*	No. 2.—*Sulphuric Acid.*
Oxide of silver.	Barytes.
Potash.	Strontia
Soda.	Potash
Barytes.	Soda.
Strontia.	Lime.
Lime.	Magnesia.
Magnesia.	Oxide of silver.

Here the order is quite reversed, for oxide of silver, the strongest base in one column, is the weakest in the other; and barytes and strontia, which manifest the most intense affinity for sulphuric acid, are found but midway among the bases arranged in order of strength for muriatic acid. Which column must be taken as representing the true order of affinities? What principle is there by which these conflicting testimonies of experiments may be brought to correspond? The answer is, that neither table is exclusively correct; that these lists, although showing the order of decomposition, and thus exhibiting to the eye, most usefully, the result of a great number of experiments, must not be supposed as strictly showing to us the order of the affinities of these bodies, unless we apply thereto a number of corrections, arising from those numerous and important causes which influence and disturb the simple action of affinity, and frequently invert altogether the results, which, if unimpeded, it would have produced.

For the chemical action of two bodies does not arise simply from their chemical affinities, but results from the combined influences of heat, electricity, cohesion, and other physical agencies, which frequently modify the chemical forces to a remarkable extent. By a change of temperature, an affinity originally weak may be made to preponderate over one previously much stronger; by electrical conditions, the strongest and most direct chemical affinities may be overcome; according as the cohesion of the acting bodies may prevail, decompositions, simple or compound, may be produced in opposite ways; and thus a chemical result is not the simple consequence of affinity directly acting, but is the resultant of a number of forces acting in different directions, and with variable intensities, of which affinity is but one, although that one which, for our object, is the most important.

It is indeed fortunate for the intellectual progress of mankind that it is so; for on the variability of the intensity with which chemical affinity may be exerted depends the existence of the infinite variety of organized and inorganic beings which people and beautify this earth. Had mere affinity been omnipotent; had those bodies which attract each other most powerfully been in all cases able to combine; and

had there been no means of dissolving their connexion when once formed, immediately on the origin of our globe, those bodies which have the most powerful affinities would have satisfied them by entering into eternal union; those next in power would subsequently have satisfied their tendency to combine, and long since all nature would have been arranged into some few chemical combinations, the breaking up of which could not be accomplished by any existing force. The complex changes of animal and vegetable digestion and respiration could not go on; the working of the metals, the chemical arts of civilized life, could not have been invented; and the planet which we inhabit would have revolved in space a barren and uninhabitable ball.

The action of these modifying causes may be easily exhibited by one or two examples. It has been already described how a solution of muriate of lime is decomposed by carbonate of ammonia; carbonate of lime being precipitated, and muriate of ammonia remaining in the liquor; but if, in place of bringing these substances into contact in solution, they be brought to act on each other at a high temperature, the result is exactly the reverse. If muriate of ammonia and carbonate of lime be heated together without water, carbonate of ammonia is found to be sublimed, and muriate of lime remains behind. If watery vapour be brought into contact with metallic iron heated to bright redness, it is decomposed, one of its constituents, oxygen, combining with the iron, the other, hydrogen, being set free; here evidently the affinity of iron for oxygen is greater than that of hydrogen. But if oxide of iron be heated to redness also, and hydrogen gas be passed over it, the oxygen is totally removed by the hydrogen in the state of water, and metallic iron is set free; here the order of affinity is exactly the reverse, and we shall soon discover the cause to which it must be attributed.

The philosopher who first declared that the order of decomposition was not the order of affinity, and pointed out the importance of attending to the other forces that modify it, was led by his observations to assert that the power to which we have attached so much importance, elective affinity, had no real existence; he said that chemical union differed from mechanical cohesion only in being exerted between the particles of different substances, and that in all cases where certain bodies combined in preference to others, the source was to be found in the accidental and external circumstances. On his ideas, the force by which the particles of a fragment of sulphate of soda are united, differs from the force by which the sulphuric acid is united to the soda only in the fact that the cohesion unites particles of the same kind, while affinity unites particles of different kinds. A salt dissolved in water is thus held in solution by chemical attraction. Two pieces of lead which adhere together are retained by mechanical cohesion; but if a piece of lead adhere to a piece of tin, or a drop of water to a surface of glass or metal, the union should be attributed to chemical affinity. It will be seen hereafter that a great deal of this peculiarity of view arose from the principle of indefinite chemical combination, which, although supported by the amazing talents of Berthollet, has been finally and totally given up. We do not now consider such phenomena as solution to be produced by chemical affinity, for we require that a chemical compound should have parted with the properties of its constituents, and acquired peculiar properties of its own, in order to prove its title to the name.

But it is still by no means easy to fix upon the limits beyond which the change of properties must pass. A change of state of aggregation is one of the most common evidences of chemical combination, as where muriatic acid and ammonia, both gases, become solid; oxygen and hydrogen, both gases, become liquid; water and bichloride of tin, both liquid, become solid, and innumerable other

cases. The production of heat, and often light, is one of the most universal attributes of chemical action; and hence for many ages the explanation of the phenomena of combustion included all that was of importance in the philosophy of chemistry. A change of volume is also very frequent, though not so universal; and consequent on this change of volume, a change, generally an increase, of the specific gravity of the body from the mean specific gravity of its constituents; thus, when oxygen and nitrogen unite to form nitrous oxide, the volume of the compound is but $\frac{2}{3}$ of that of the mixed constituents; when nitrogen and hydrogen unite to form ammonia, the resulting volume is but $\frac{1}{2}$ of that of the gases mixed before combining; if 100 volumes of alcohol be mixed with 100 volumes of water, the mixture will occupy but 196 volumes; and on mixing similar quantities of water and oil of vitriol, the resulting volume is but 185. Change of colour also frequently occurs; but in all these cases, although such marked results indicate an intimacy of union that can scarcely be explained by mere cohesion, yet other physical forces may intervene, and in addition to the evidence of chemical action already stated, the most important and necessary still remains, change of chemical properties.

I have on several occasions mentioned change of properties as characteristic of chemical combination, but it may be proper here to enter into a few detailed examples of its nature and its source Chemical affinity is not a single force, giving to all bodies within its influence the same properties, though it may be in different degrees. On the contrary, the power which confers upon bodies their chemical properties is of two kinds, antagonistic to each other, and such that, by acting with equal energies, their effects are mutually destroyed. Gravity, in acting upon bodies, acts upon all bodies in the same manner; the molecular forces, which determine the hardness, the ductility, the solid, or liquid condition of bodies, may make one body more or less hard or ductile than another, or they may render one body solid and another gaseous; but it is not in the nature of cohesive forces to render the hardness of one body opposite to the hardness of another, so that together they shall produce softness. Yet such is the nature of the sources of chemical activity; thus sulphuric acid and soda are actuated by affinities for each other; the same force which gives to them their tendency to combine, gives to one the properties of an intense acid, and to the other the character of a powerful alkali; yet these forces are so peculiarly related to each other, that, when the bodies have combined, the acid and the alkaline properties disappear, and there results a substance, formed by their union (Glauber's salt), innocent, inactive, with little tendency to combine, destitute of chemical affinity for other bodies, yet containing in itself constituents which may be again set free, and exhibited with all their active properties.

The force of chemical affinity is therefore exerted only between bodies possessing opposite qualities, and by their union a substance is produced possessing qualities which are not the mixed qualities of its components. The forces which produce cohesion and solution are found most active where the resemblance between the bodies is most complete. Thus metals adhere most powerfully to

other metals, and for their solution, mercury, a liquid metal, can alone be used; salts dissolve in water always most easily when they show their resemblance to it by already containing water of crystallization in their mass; inflammable bodies, as sulphur and phosphorus, do not dissolve in water, nor in acids, but in liquids, themselves inflammable, as ether, sulphuret of carbon, and the oils; camphor, the resins, the fatty matters, require also, for their solution, fluid menstrua of analogous, oily, and spirituous natures. It is the contrary with chemical combination; the more complete the opposition of properties may be, the more intense is the affinity by virtue of which combination is effected: a metal combines with oxygen or chlorine: ether, or a metallic oxide, combines with the acids to form salts. In all these cases the opposition of properties is the cause of the chemical affinity, and the neutralization or change of properties is its effect. Thus the gases, ammonia, and muriatic acid, a caustic alkali, and an intense acid, form the solid sal ammoniac, a neutral salt, destitute of the active properties of its constituents: thus carbon, hydrogen, and nitrogen, elements of our daily food, combine to generate the most active poison that has been found, the prussic acid; and this prussic acid, by farther combination with oxide of iron and with potash, may generate a yellow salt, which is perfectly without action on the living body, and which, under the name of ferro-prussiate of potash, is of daily extensive employment in the arts.

The elements which, mixed together, constitute our atmospheric air, combined in one proportion, form a gas which, when breathed, produces agreeable intoxication (nitrous oxide); in other proportions, a deep orange-coloured gas (nitrous acid), which, by intense cold, may be obtained liquid; and in an intermediate form, a gas colourless and transparent (nitric oxide), which, when mixed with air, produces, by combining with its oxygen, the nitrous acid. In all these cases new properties are assumed, the characters of the constituent elements furnishing no means of predicting the properties of the compound.

This clear distinction between chemical affinity and cohesion was not perceived by Berthollet; and hence, misled by the supposed existence of compounds which connected together the extremes of chemical and mechanical force, he advanced the principle that the differences observed between them arose solely from external circumstances. This principle has been rejected; but the discussion to which it was subjected showed the importance of attending to the influence which external circumstances really do exercise, and which is frequently, in practice, more powerful than the force of affinity itself. It is therefore necessary to study in detail the influence of the external physical agents upon chemical affinity.

1st. *Influence of Cohesion.*—A diminution of cohesive power among the particles of one body, allows those of another to come into closer approximation to them, and favours the chemical action of the two bodies. Thus the ancient chemists expressed the influence of cohesion by the Latin proverb: *Corpora non agunt nisi sint soluta;* bodies do not act unless they be dissolved. And of all forms of matter, liquidity is that in which chemical action is most rapid and most energetic.

There are many instances of bodies acting on each other, although in the solid form. Thus, when chlorate of potash and sulphur, or chlorate of potash and sulphuret of antimony, are rubbed together, the mixture explodes from the rapid decomposition which ensues. When fulminate of silver, or iodide of amidogen, is even slightly touched, detonation follows. In these cases, the original arrangement of particles must have been so instable, that the imperfect approach produced by mechanical mixture, or the slight change of position arising from a sudden shock, was sufficient to cause a new mode of combination. But, if such cases as these be considered as exceptions, we may look upon solid bodies in general as being without chemical action on one another.

In the gaseous form of matter, chemical affinity appears to be controlled and weakened by the mutual mechanical repulsion of the gaseous particles. Thus, oxygen and hydrogen, bodies whose affinities are so strong, may remain in contact as gases for an indefinite period. Nitrogen and hydrogen have no apparent tendency to unite when mixed. Hydrogen, in the form of a gas, is without action on carbon, or arsenic, or phosphorus, although under other circumstances it unites with them, forming characteristic bodies. In order to obtain the full chemical action of gaseous bodies, they must be brought into play at the moment of their being set free or formed; in their *nascent state*, as it is termed. It may well be, that, when water is decomposed and hydrogen is liberated, there is a moment before the hydrogen actually assumes the permanently elastic form; and being then, perhaps, liquid, and in a highly concentrated condition, its affinities are manifested with extraordinary force. It is the same with other gases; they act always with their full power only in their nascent state.

The influence of cohesion in determining chemical action is, however, of much greater importance in another way, as serving, upon the principles of Berthollet, to explain the anomalous discordance between those experiments upon which the tables of the affinities of bodies for each other had been constructed. Thus it has been shown, that in a table of affinities of the bases, oxide of silver would appear to be the strongest base if we used muriatic acid: barytes should be looked upon as the most powerful if sulphuric acid had been employed; while, if the relation of the bases to nitric acid were taken as the standard, potash would be found to excel the others. In such cases, the diversity is to be ascribed to the influence of cohesion; and in all cases of the mutual action of various bodies in solution, the result is found to be the formation of such compounds as are least soluble.

Let us imagine a quantity of sulphate of soda and nitrate of potash to be dissolved in water. Each acid is attracted at the same moment by both bases, and each base by both acids, so that there occurs a division of each acid between the two bases, and of each base between the two acids. There are thus in solution sulphate of soda and sulphate of potash, nitrate of soda and nitrate of potash; and while the solution is dilute, all remain so; but if the liquor be very much concentrated, the sulphate of potash, being a sparingly soluble salt, is deposited in crystals, and a new distribution takes

place in the mother liquid. Supposing all sulphate of potash removed, and that there remain sulphate of soda, nitrate of soda, and nitrate of potash, the remaining potash divides itself again between the acids, and a new portion of sulphate of potash is formed, which, by a new crystallization, may be separated. In this way, according as the evaporation is continued, new quantities of sulphate of potash are consecutively formed, until there remains in solution neither potash nor sulphuric acid, but only soda in combination with nitric acid. Here, then, supposing the chemical affinities of potash and soda, of sulphuric and of nitric acids, to be exactly equal, the decomposition which actually occurs, and the manner in which it really takes place, are explained perfectly by the greater cohesion of the sulphate of potash, and its consequent sparing solubility.

In like manner, ordinary hard water contains soda, muriatic acid, lime, and sulphuric acid. The soda is certainly the stronger base, and the sulphuric the stronger acid; and yet, on evaporating such water, the salt which first crystallizes is sulphate of lime; and on continuing the evaporation, all sulphuric acid may be removed in combination with the lime. But the acids and bases being divided among one another in solution, there coexist sulphate of lime, sulphate of soda, muriate of lime, and muriate of soda. But when the liquor is concentrated, the sulphate of lime is first deposited, and a new quantity being formed, all its constituents are eliminated in combination, precisely as the sulphate of potash was separated in the former case.

In these instances the separation of the least soluble ingredients took place by degrees, and, as it were, artificially; but if any one of the substances produced be perfectly insoluble, it is at once and in full quantity expelled. Thus, when we mix together solutions of nitrate of barytes and sulphate of soda, there is instant formation of sulphate of barytes, and the solution contains only nitrate of soda. But even here, although the formation of the sulphate of barytes appears instantaneous to the senses, it yet may, in point of fact, be just as gradual as in other cases. Thus there may have been a moment after mixing the solutions when there were present, dissolved together, nitrate of barytes, nitrate of soda, sulphate of soda, and sulphate of barytes; in the next moment the latter precipitates, and the barytes in solution, still dividing itself between the two acids, another quantity is formed. This then precipitates, and thus, in a space of time that is too small to be detected, the quantity of barytes in the solution is reduced to the mere trace of sulphate which the quantity of water can dissolve, and which is too small to be detected by our ordinary tests.

The nature of double decomposition depends thus on the relative solubility of the compounds formed. In whatever way the most insoluble bodies may be generated, the decomposition occurs. It is thus that, on mixing solutions of carbonate of ammonia and of nitrate of lime, there are formed carbonate of lime and nitrate of ammonia; not merely that the divellent affinities were more powerful than the quiescent forces, but that the insolubility of the carbonate of lime produced its separation from the liquid, and hence the union of the substances which compose it.

The inversion of affinity which is produced by the influence of cohesion is not limited to cases of double decomposition. There is no doubt but that acetic acid is a stronger acid than carbonic acid; and on adding acetic acid to a solution of carbonate of potash in water, the carbonic acid is expelled, and acetate of potash formed. Yet, if a stream of carbonic acid gas be passed into a solution of acetate of potash in alcohol, the salt is decomposed, acetic acid being set free, and carbonate of potash formed. The cause of this is the insolubility of the carbonate of potash in alcohol; for, on the first action of the carbonic acid, the potash divides itself between the two acids, and there is formed some carbonate, which is thrown down; then another quantity, which also separates, until ultimately all is precipitated, and thus one of the feeblest acids may overcome the affinities of another which is much stronger.

By this principle of distribution of acids and bases, we are thus enabled to account for a variety of facts, which appear totally opposed to affinity, if it were not subject to such modifications; but, although it is so convenient for explanation, it should not be admitted as a principle in science if there could not be adduced evidence of its actual and independent truth. That it does occur in many cases cannot well be doubted; thus the solution of sulphate of copper in water is of a rich blue colour, and that of muriate (chloride) of copper of an emerald green. Now, on mixing muriatic acid with a solution of sulphate of copper, the blue solution is immediately changed to green, showing that the weaker acid has divided the oxide of copper with the stronger, although, so far from precipitation occurring, the new compound is the more soluble of the two. Also, on mixing a solution of sulphate of iron with sulpho-cyanic acid, the liquor becomes intensely blood-red coloured, showing that a quantity of sulpho-cyanide of iron has been formed, although the sulpho-cyanic acid is much weaker than the sulphuric, and no precipitation occurs to favour its production.

These, and many other such examples which might be brought forward, show that the opinion of Berthollet, that the acids and bases, when mixed together in solution, arrange themselves so that each base shall be divided among all the acids, and each acid among all the bases, is in a great many cases true, and that it is one of the most fruitful sources of the decompositions which occur in our experiments; but it remains to be decided whether it is universally true, and whether, if all acids and bases act thus equally on one another, we should abandon the idea of chemical affinity being elective.

The answer to this question has been long since received in science. The principle of Berthollet does not hold always, for numerous instances may be produced where this partition of acids or of bases does not take place. Thus boracic acid and sulphuric acid both redden litmus, but the former colours it of a port-wine colour, while the latter tinges it of the red of an onion-skin. If a quantity of borax (borate of soda) be dissolved in water coloured blue by litmus, and some sulphuric acid added thereto, the liquor becomes coloured wine-red from free boracic acid; but, although the slightest trace of sulphuric acid in excess would show itself by

changing the red to that of the onion-skin, no sign of it is found until all the boracic acid has been expelled. Here, therefore, there is no partition of the base between two acids; all the sulphuric acid which is added unites with the soda, and all the boracic acid is ex pelled. If a solution of carbonate of soda be coloured blue by litmus, and sulphuric acid added, it may also be shown, by the ab sence of the peculiar red which free sulphuric acid gives, that there is no division of base between the two. The carbonic acid is totally expelled, and the sulphuric acid combines exclusively with the soda. If the solution be dilute, the carbonic acid remains dissolved in the liquor; if it be concentrated, it is evolved in the gaseous form; that makes no difference.

Affinities are not, therefore, as Berthollet considered, all the same in power. The framers of the tables of affinity were right as to the general principle, that different bodies have different degrees of affinity for each other; but they erred in supposing that they could construct a table for the absolute order of affinities.

To sum up the details that have been given of the influence of cohesion on the affinities of bodies acting on each other in solution, it may be said that, 1st, In almost all cases of precipitation, the nature of the double decomposition is determined much more by the fact of one of the bodies formed being insoluble, than by the resultant of the united affinities of the bodies which are engaged. 2d, That where there is no separation of an insoluble or of a sparingly soluble compound, the acids and bases, if they differ very much in energy, are exclusively united, the strongest acid with the strongest base, and the weakest acid with the weakest base; and if there be not base sufficient to neutralize all of the acids, a corresponding quantity of the weakest acid being left out of combination altogether; but, 3d, That if the acids and bases be not very different in energy of affinity, they arrange themselves in such a manner that each base shall be divided between all the acids, and each acid divided between all the bases, in proportions which depend upon the quantities of each acid and of each base that may be present, and on its affinitary force. Thus, if there be two acids and two bases present, there will be four salts; if three acids and three bases, nine different salts; and generally, the number of compounds in solution will be equal to the whole number of acids multiplied by the whole number of bases present.

2d. *The Influence of Elasticity.*—The absence of cohesion, or, still more, the substitution for cohesion of its antagonist power repulsion, as shown by the property of elasticity in the form of gas or vapour, modifies chemical affinity in a perfectly analogous manner to that which has been already described; for, precisely as the formation of an insoluble substance in a liquid will enable lower degrees of affinity to preponderate by removing the body which is formed by its insolubility, so will repulsion or elasticity determine the production of such substances as by their volatility may be driven off, even though the affinities of their elements may be much feebler than those of other bodies. In all such cases the same principle of distribution, so fully described already, may be supposed to hold: thus a solution of sulphate of magnesia is perfectly

decomposed by ammonia, the magnesia being precipitated; but, on mixing sulphate of ammonia with dry magnesia, and applying heat, the ammonia is expelled, and the sulphuric acid remains, united exclusively with the magnesia. Supposing that there is little dif ference between the affinities of these two bases for sulphuric acid, the acid in the mixture may be divided between the two; in each case there is free magnesia and free ammonia, for the acid is only able to saturate a part of each. In the solution the excess of magnesia is insoluble, and it is expelled; in the dry way the excess ot ammonia is gaseous, and it is driven off; and thus, with the same substances and the same affinities, precisely opposite decompositions are produced by the influence of cohesion and elasticity. The decomposition of muriate of lime by carbonate of ammonia in solution has been already noticed, where carbonate of lime is formed in consequence of its insolubility. If the carbonate of lime and the muriate of ammonia so produced be dried and heated, the precisely reversed decomposition will take place; there are at first produced muriate and carbonate of lime, muriate and carbonate of ammonia; and this latter, being volatile at the high temperature which is used, is driven off, and new portions formed until the interchange of elements is complete.

The boracic acid has been already noticed, as being one so feeble in its affinities that the law of the division of acids and bases does not hold with it, but that sulphuric acid can deprive it of every particle of base. This is quite true as long as these acids are in the liquid form, but at a high temperature the reaction is reversed. If a mixture of sulphate of soda and boracic acid be heated to redness in a crucible, the sulphuric acid will be driven off in consequence of its volatility, while the fixed boracic acid will remain combined with the whole quantity of base. The white, inert, earthy substance, silica (powdered flints), the acid properties of which are so feeble that it is only from analogy that it is recognised by chemists to be an acid, may, at a high temperature, expel the most powerful acids from their combinations; thus the commonest sort of pottery is glazed by throwing over it, when at a bright red heat, handfuls of common salt; this is instantly decomposed; the silica of the earthy material of the vessels combines with the soda of the common salt, and the muriatic acid is driven off in white clouds of elastic vapour. Here the acid, which is the feeblest when dissolved in water, may expel the strongest when the temperature is raised; and admitting that in the commencement a partition of the base between the two took place, even to a very small extent, the final and complete expulsion of the more volatile must result.

From the great variety of compounds into which water enters, it is easily expelled, not that it is inferior in affinity to most other bodies, but from its greater volatility. We shall hereafter see reason for looking upon water as being a base of considerable force, and entering into combination in forms which should possess consider able stability; but when a compound of water is subjected to heat, the elasticity of the water diminishes its affinity so far that it may easily be expelled.

The elasticity which certain elements possess when free, may be

a cause why the compounds which they form are easily decomposed by heat, if their actual affinity to one another be not considerable. Thus the nitrate of barytes, which contains nitrogen and oxygen in combination with barytes, gives, when heated, a mixture of nitrogen and oxygen gases: nitrate of lead gives, when heated, pure oxygen and nitrous acid fumes. Chlorate of potash, by a high temperature, abandons all its oxygen gas; and the remaining elements, having a powerful affinity for each other, resist the increase of heat, and remain as chloride of potassium.

When the decomposition of a body by heat is thus determined by the elasticity of one of its constituents, it is necessary, for the success of the process, that this constituent should be allowed freely to escape. If it be forced to remain enveloping the residual substance, the decomposition ceases. Thus, by heating carbonate of lime to redness, it is resolved into lime and carbonic acid; but if the carbonic acid be not removed, the decomposition would immediately cease, and the carbonate of lime might be melted without being decomposed. The removal of the carbonic acid is accomplished, in burning lime on the large scale, by the limestone being heated in a kiln, through which there is a continuous draught, by which the carbonic acid is carried off according as it is formed. The necessity for the removal of the carbonic acid may be shown by placing bits of white marble in a porcelain tube, heated to redness in a furnace, connected with a pneumatic trough, and fitted to a retort at the other end, by which steam may be passed into the tube; at first scarcely any carbonic acid is set free; but, by keeping up a supply of steam, the gas is rapidly produced, and the lime becomes very soon completely caustic.

It is in this way, also, that we may explain the contrary order of decomposition that may be produced by oxygen, hydrogen, and iron. If metallic iron be in the tube, and the latter be kept full of steam, every particle of hydrogen which is formed is carried off; and there being then a space provided into which the hydrogen can easily spread itself, the steam will be decomposed, and the iron converted into oxide. If, on the contrary, the tube contain oxide of iron, and be kept full by a current of hydrogen gas, there is presented to every molecule of steam produced room for its escape; and the formation of steam being thus favoured by its elasticity being allowed full play, the reduction of the metal is completed.

Independent of its influence on cohesion, a change of temperature is capable of modifying the affinities of bodies in a remarkable degree. Thus charcoal is not capable of being melted or vaporized, and yet, although at ordinary temperatures quite inert, few bodies can resist its deoxidizing action at a red heat. Bodies which take fire when heated do so in consequence of their affinity for oxygen being augmented by the increase of temperature. The action of the electric spark in producing the explosion of gaseous mixtures, depends on its heating very much the few particles of gas which lie immediately in its path, and the combustion being communicated by them to the general mass. The affinities of bodies for each other appear to be thus exalted by the agency of heat in many cases, but the exaltation does not appear to be the same for all. Heat appears

often to diminish the affinity of bodies; thus the explosion of de tonating compounds was so explained; but this appears to arise from the heat really exalting the affinity of the more powerful constituents, so that new and more permanent bodies may be formed: thus fulminating silver explodes, not that its elements may separate, but that bodies of a more permanent constitution may be formed The iodide and chloride of azote were looked upon as being examples of mere separation of elements on the application of heat; but Marchand and I have found that these bodies contain hydrogen, and that they are decomposed in consequence of the formation of hydrochloric or hydriodic acid. To produce many bodies of instable nature, it is necessary to avoid the use of heat; not that heat diminishes the affinities of their elements in general, but that the heat enables those elements to satisfy their affinities better, by combining in a more stable form.

It has been mentioned that Berthollet considered affinity as being not elective, but that the combination of one body to another was determined by the circumstances under which they were placed; and that, in cases where many bodies of equal solubilities existed together, they were divided among one another in proportion to their masses; but he in this case introduces a term which has caused great difficulty in the discussion of the doctrines which he advanced. He says that the bodies mixed together combine, not only in proportion to their masses, but of their affinities; and hence might appear to admit that bodies had different degrees of affinity, and that this might, therefore, be elective; but, if I conceive his opinions rightly, the affinity of which he spoke was not the force to which we assign the power of choice of one body over another, but he carried on the analogy to cohesion, and considered that the affinity of one body, A, to another, B, might be greater than to a third, C, not so as to make A unite with B in preference to C, but that, when it had been united with B, it would hold it more firmly than it could retain C. This is like what is found with cohesion; if several bodies be placed beside each other, they show no power of elective cohesion; but if they be brought into actual close contact, the degree of cohesion may be different for each. It is in this way that Berthollet recognises a difference of affinity, and hence the obscurity that is often ascribed to his statement of his views, from the sense which he attached to the word affinity being mistaken.

We owe to this philosopher an attempt at measuring this power of affinity, which, though incorrect, yet, as being one of the first steps made towards numerical laws in chemistry, deserves notice. He looked upon the neutralizing power of a body as being the measure of its affinity for another, and considered that the deviations from this rule arose from the influence of cohesion or of elasticity: thus the same quantity of potash is saturated by

Sulphuric acid	40 parts.	Muriatic acid	36·5 parts.
Nitric acid	54 "	Acetic acic	51 "
Carbonic acid	22 "	Oxalic acid	36 "

Hence, if mere affinity was allowed to act, carbonic acid should be the strongest, and nitric acid the weakest in the list; in like manner, the same quantity of sulphuric acid neutralizes

Potash	48 parts.	Lime	28 parts.
Soda	32 "	Barytes	76 "
Ammonia	17 "	Magnesia	18 "

and ammonia and magnesia should be the strongest of all bases, were it not for the insolubility of the one and the volatility of the other body.

These numbers, which are now known as expressing the quantities of substances that are equivalent to each other in combination, are fully recognised as totally independent of the force of affinity exercised by each body. As yet we have no other measure of affinity than the order of decomposition, controlled by the estimate of the influence which cohesion and elasticity may exercise. From the electrical relations of bodies, attempts have been made to estimate the relative affinities of chemical substances, the results of which will be described in their proper place.

Of the Influence of Light on Chemical Affinity.—Although attention has latterly been very much directed to the influence of light on chemical affinity, from the accidental discovery of some very remarkable circumstances connected with it, yet there have not been discovered as yet any general principles to which those results can be reduced; and the greater number of the investigations that have been made are occupied by experiments of detail, which, from their want of connexion and their multiplicity, cannot be successfully contemplated from any general point of view at the present moment. So far, however, as positive facts have been discovered, and as even plausible explanations of those facts have been suggested, I shall endeavour to represent, briefly, the actual condition of our knowledge of this department.

In many cases, bodies which in obscurity remain totally without action on one another, are brought into combination by exposure to light, and the rapidity of their reaction is proportional to the brilliancy of the light. Thus chlorine and hydrogen mixed remain unaltered for any period in the dark; if exposed to the diffuse daylight, they silently combine, but explode suddenly if a direct ray of sunshine fall upon the mixture. Chlorine dissolved in water, if kept in the dark, remains a long time unaltered, but if exposed to sunshine, is rapidly converted into chloride of hydrogen, water being decomposed, and oxygen eliminated in a gaseous form. Chlorine unites with carbonic oxide only under the influence of light, whence the name Phosgene, a *light-formed* gas, was given to the compound by its discoverer, Dr. Davy. Chlorine and sulphurous acid unite also only when exposed to brilliant sunshine; so much so, that in Dublin but few days in summer are found bright enough to form it. The decomposing action of chlorine, iodine, and bromine upon organic bodies, which consists in the separation of hydrogen, and the assumption generally of a corresponding quantity of chlorine, &c., in its place, is regulated also in a remarkable degree by the brilliancy of the light under which this operation is carried on. Thus, even in summer, in Dublin, I never could deprive acetone of more than one third of its hydrogen, forming from $C_3\, H_3\, O.$, the body $C_3\, H_2\, Cl.\, O.$; but in Paris, in summer, the chlorine removed another equivalent of hydrogen, and Dumas and I succeeded in obtaining the body $C_3\, H.\, Cl_2\, O.$ In like manner, in bright sunshine, the action of chlorine on pyroxylic spirit is so violent, that unless the vessel be carefully shaded, the decomposition proceeds by a series of explosions, while I have found it exceedingly difficult in gloomy weather to produce any action whatsoever. Instances of this kind might be very much multiplied, but those described are sufficient to point out the general manner in which light is found to act.

The action of light appears occasionally limited to the simple separation of bodies previously combined. Thus colourless nitric acid, when exposed to sunshine, evolves oxygen gas, and becomes coloured yellow from nitrous acid which remains. The fading of Prussian-blue patterns on cotton, which Chevreul found to depend on the escape of cyanogen, and the conversion of the blue into a white compound, containing less cyanogen, is also an example of this principle.

Setting aside, for the present, the influence of light on the production of colouring matters in organic bodies, which will be described as a portion of the chemical history of the individual substances, I shall now only advert to the action of light upon the compounds of the easily-reducible metals, particularly silver, by the study of which such remarkable results have latterly been obtained.

Scanlan first showed that, when nitrate of silver blackens under the influence of light, its decomposition is produced by organic matter, as by contact with paper, or by the organic substance, which even distilled water contains in small quantity. Chloride of silver also is affected by light only when in contact with organic matter or with water, and in the latter case, also, most probably from acting on the organic matter which the water held in solution. When oil of vitriol is poured over chloride of silver, this is not altered by the light, the sulphuric acid combining with the water, and probably destroying the organic matter therein dissolved. I apprehend that in most, if not all cases of the decomposition of a metallic salt and the reduction of the metal under the influence of light, a substance containing hydrogen, exclusive of the water of solution, must come into play.

The decomposition of the salts of silver in contact with paper under the influence of light, has become of interest to the arts as a process of obtaining accurate outlines, and is called *photography*, or *photographic drawing*. If a sheet of paper be washed with a very dilute solution of chloride, iodide, or, better, bromide of potassium, and then with a solution of nitrate of silver, there is formed in the substance of the paper chloride iodide, or bromide of silver, which, being in contact with abundance of organic matter, is blackened by a very short exposure even to moderate light. If an opaque body be laid between a sheet of such paper and the light, the portions to which the light arrives become dark, while that under the object remains white, and thus the most delicate and complicated outlines of foliage or fibres may, by a few minutes' exposure to the solar rays, be fixed upon the paper with a degree of accuracy inimitable by the hand. To render such a drawing permanent, it is necessary to remove the silver compound under the pattern; for if it remained, the blackness would gradually become uniform over the entire surface, and the picture would be effaced. This is effected by washing the paper, after the image has been completely formed, by a solution of some substance capable of dissolving out all of the undecomposed salt of silver; for this purpose, ammonia, hypo-sulphite of soda, and strong solution of common salt are those generally employed.

The most remarkable features connected with the chemical agencies of light result from the recent experiments of Herschel. He

has shown, as was slightly noticed when describing the general characters of light, that the chemical effects are not regulated by, nor limited to the luminous spectrum, but by totally distinct rays, which, according to the substance employed to show their decomposing action, may extend far beyond the visible limits on either side, or may stop short in the middle of the coloured space; and that the greatest effect, which generally occurs at the violet extremity of the spectrum, may be produced at other and widely-distant points.

A singular, and at present unaccountable, consequence of the action of the prismatic spectrum on paper impregnated with chloride of silver is, that the spaces on which the coloured rays fall become coloured, acquiring a tint corresponding to that of the light incident upon them, so that the spectrum fixes its own image on the paper. Thus the colours impressed were in one experiment:

Spectrum Colours.	Colours formed on the Paper.
Extreme red.	None.
Mean red.	None.
Orange.	Faint brick red.
Orange yellow.	Brick red, pretty strong.
Yellow.	Red, passing into green.
Yellow green.	Dull bottle green.
Green.	Do., passing into bluish.
Blue green.	Very sombre blue.
Blue.	Black, passing into metallic yellow.
Violet.	Do. Do.
Beyond the violet.	Violet, or purplish black.

It is in the lavender-coloured space that the chemical effects are generally most intense; when the light of it had been concentrated by a lens, and received on a piece of prepared paper, the blackening was instantaneous, precisely as if a red-hot body had been applied behind, or a smoky flame directed on the paper over all the space illuminated, and accurately marking its outline.

In the table of impressed colours just given, the red rays appear to have produced no effect; but they are by no means destitute of action. When a quantity of diffused light is allowed to fall upon the paper, in addition to the more brilliant spectral colours, the chemical image is found to acquire a pure white prolongation beyond the red space, in which the darkening action of the diffuse light appears to have been suspended. The opposite extremities of the spectrum appear, therefore, to have different powers, the darkening quality of white light being due to the difference between the two in favour of the violet end; and it is probable that by a balance of action, a sensitive paper might be exposed to the action of united beams of brilliant violet and red light, and remain perfectly unaltered in its colour. Herschel did not, however, succeed so far: paper blackened by violet light has that blackness removed by the action of red light upon it; but it was found impossible to catch the point where the paper should be white; for, according as the black of the violet end passed off, the red impression was substituted for it. When, however, the different coloured rays were made to fall simultaneously on the paper, the neutralizing power of the opposite ends of the spectrum was beautifully shown. The blackening power of the more refrangible rays was suspended over all the space

upon which the less refrangible rays fell, and the shades of green and sombre blue, which the latter would have impressed upon a white paper, were produced on that portion which, but for their action, would have been merely blackened.

The paper with which those results were obtained derived its sensibility to light from chloride of silver; but the action of other salts of silver gives such anomalous and variable effects, that no general principle whatsoever can be deduced from them; thus, with bromide of silver, the blackening proceeds uniformly over the whole of the visible spectrum, and the whitening effect is produced beyond it to a considerable distance. The subject has been shown by Herschel to be one of considerable importance and great extent; and from the popular interest it excites, some clew to a more general knowledge of its principles will probably be soon obtained.

The process lately discovered by Daguerre, of fixing the images of external objects upon a prepared metallic plate, is one which also deserves attention, as being founded upon the chemical agencies of light, although hitherto there has been but little success in the attempts made to assign a theory of it. It is not complicated in detail. A plate of silvered copper is cleaned with dilute nitric acid, so that the surface of silver may be absolutely pure, and is then exposed to the vapour of iodine until a gold-coloured pellicle of iodine of excessive tenuity is deposited upon it. In this state it is very sensible to light. The plate so prepared is placed in a camera-obscura, and the image of the object required is allowed to remain on it for a space of time, which varies with the brightness of the light. When it has been sufficiently exposed, it is removed, and submitted to the action of the vapour of mercury, by which the picture is rendered visible. As there still remains, however, a general sensibility to the farther influence of light, this is removed by dissolving away all the iodine and iodide of silver by a solution of hyposulphite of soda. The shadows remain then marked by smooth amalgamated surfaces, and the lights, by the corresponding portions being of a dull gray colour, possessing only a power of diffuse reflection.

The explanation of this process, which, from my own observations, I am disposed to suggest, is, that the iodine combines with the silver, and forms iodide of silver, which is spread in an amorphous state, forming an excessively thin layer, like varnish, over the surface of the plate. Under the influence of the light, I consider that this crystallizes as melted sugar does, but so minutely as to be invisible to the eye, and the closeness and completeness of the crystalline structure being proportional to the duration and intensity of the light to which it had been exposed. When, then, the vapour of mercury attacks the plate, the iodide of silver in both conditions is decomposed, and the iodine being replaced by mercury, an amalgam of silver is formed, uniform in surface, and perfectly metallic in its lustre, over the shaded portions; but the crystalline iodide, in being decomposed, gives a crystalline amalgam, which, from the minuteness of its particles, presents only a grayish tint, and, being mixed with interspersed points of bright, smooth amalgam where the light had been less powerful, shades off proportionally all the intermediate effects.

The application of the mercurial fumes cannot be pushed far enough to decompose all the iodide of silver, for it would injure the picture by depositing itself irregularly and in excess. It is therefore necessary, as soon as enough has been acted on by the mercury to bring out the picture in a distinct manner, to remove the remainder by the washing which has been described.

The influence of colour on the production of pictures by Daguerre's process is very marked; the images of green objects are scarcely at all defined, so that the method is scarcely applicable to

taking landscapes. Red and orange are also very feeble in their effect; but blue, even so intense as to be not at all bright, is more powerful than a brilliant white light. In order, therefore, to produce good effects, objects should be selected either white, or of colours from which red and orange should be absent. The fixation of colours in a manner similar to that discovered by Herschel, and already noticed, has been remarked in Daguerre's process, although so irregularly that no advantage has as yet been taken of it for technical uses; but I have myself seen, on more than one occasion, where a deep blue sky was interspersed by patches of bright white clouds, a perfect picture of the sky in its natural colours to be formed upon the plate. Time-worn stains, and marks upon the surface of stone buildings, are also occasionally represented in their natural colours. In the majority of cases, however, where colours are produced upon the plate, they do not correspond in position or tint to those of the natural objects whose image had been obtained.

[Since the preceding paragraphs were written by Dr. Kane, numerous improvements have been made in this beautiful chemical art in America and elsewhere: the theory of the process is also much better understood. The most important of these improvements is the application of Daguerre's process to taking portraits from the life. This is due to Dr. Draper, who succeeded with it soon after the French process was known in this country. At first the direct or reflected rays of the sun were required; but modes of preparation, giving the plate more sensitiveness, have been since discovered, so that the ordinary diffused light of day is now sufficient.

The best process for obtaining portraits is as follows: The plate, having been carefully cleaned, is iodized to a pale lemon colour; it is then exposed to the vapour of bromine for a sufficient length of time to bring it to a golden yellow. It is a great advantage to keep it in total darkness for three or four hours before using it. The person whose portrait is to be taken, having been seated in a suitable chair, with a support to keep the head perfectly steady, before a window, so that the light shall illuminate all those portions seen in the camera with proper strength, the plate is to be exposed to the focal image for a time, which may be determined by previous trials.

Much of the beauty of the picture depends on the object-glass of the camera; very good proofs may be had by an arrangement of uncompensated convex lenses four inches in diameter and eight inches in focus; but the most finished pictures are obtained by the use of achromatics, which ought always to be preferred.

The process of exposing the proof to the mercurial vapour is one of great delicacy; sometimes the object is suddenly evolved, sometimes it requires the mercury to be maintained at 175° Fahrenheit for a long time. Experience alone can determine when the full effect has been obtained.

After the picture has been brought out, and the coating of iodide of silver removed, it remains only to effect the gilding. This is accomplished by pouring all over the silver surface a very weak solution of the chloride of gold in hyposulphite of potash, and warming it gently with the flame of a spirit-lamp. At a particular temperature, the shadows increase in depth and the lights in brillancy; the plate is then to be thoroughly washed. The gilding serves to render

the picture immovable by ordinary exposure or accident, and imparts to it a beautiful satiny lustre, and chatoyant play of colour.

The great difficulty in the management of the Daguerreotype lies in the circumstance that the iodide of silver is not affected correspondingly by lights that are of different degrees of brilliancy, if they should be of different colours. And it is only under particular circumstances, not easy to reproduce, that lights of the *same* colour, but of different strengths, produce a corresponding degree of whiteness on the plate. Often, when the light is too active, the proof takes on an unpleasant slate-blue colour, from the exterior portions of the iodide assuming a state of solarization before those beneath have had time to undergo change; a phenomenon resembling what takes place when a sheet of paper is held before a very bright fire, the exposed surface becoming scorched, while the back has scarcely had time to become warm.

As respects the theory of this process, I do not coincide with the views expressed by Dr. Kane. In the shadows no mercury exists; the lights are an amalgam. When a Daguerreotype is exposed to the vapour of mercury to bring out its picture, a decomposition of all those portions of the iodide which have been exposed to the light ensues; an amalgam is formed, and the iodine expelled unites with the metallic silver behind, effecting, therefore, a corrosion of the plate; no iodine is evolved, and for obvious reasons such an event is impossible. The light therefore imparts to those portions of iodide on which it has impinged, the quality of being decomposed at a lower temperature by the vapour of mercury than the temperature at which an unexposed iodide can be decomposed; an amalgam therefore forms on such positions when the temperature does not rise beyond 175° F., though the whole surface might be decomposed and whitened if the temperature were carried high enough.

The chemical rays which affect the iodide of silver are chiefly those of high refrangibility, and these rays manifest many habitudes resembling those of radiant heat. They are absorbed and lost in effecting the change, so that a ray of light which has once fallen on a Daguerreotype plate, and is reflected by it, has lost all its activity. Whatever, therefore, will interfere with the absorption, will interfere with the sensitiveness of different compounds. Thus it has long been known that there is a proper colour to which the plate may be brought when it possesses the maximum of sensitiveness: this is the golden yellow; when it is red, or green, or blue, it is much less sensitive; and when of a lavender colour, hardly sensitive at all. This arises from the circumstance that under these conditions the optical character of the plate is such that it *reflects* the active rays in part or altogether.

I have already remarked that lights which vary in intensity do not affect these plates in a corresponding way; this arises from the circumstance that, as the iodide of silver is undergoing change, a large quantity of light becomes latent, precisely as a piece of ice in the act of melting absorbs a large quantity of heat, not discoverable by the thermometer; this phenomenon accompanies the blueness which the compound assumes as it changes into the condition of a subiodide.]

CHAPTER VII.

OF THE LIGHT AND HEAT DISENGAGED DURING CHEMICAL COMBINATION.

It has been already noticed that the union of substances having chemical affinity for each other is accompanied by increase of temperature; and in cases where the affinity is powerful, the effect may be so great that the bodies shall become luminous: in such instances the chemical action is said to be accompanied by *combustion*. In considering the relations of this phenomenon to affinity, it will be necessary to notice, first, the general circumstances of combustion; secondly, the relation between the amount of affinity and the quantity of heat evolved; and, finally, the explanations that have been offered of the origin of the light and heat.

In ordinary language, a body is said to burn when its elements unite with the oxygen of the air, and form new products. The accompanying phenomena are in general those on which popular attention becomes fixed, and for which the process is generally carried on; and hence, to the world at large, combustion is of importance only as a source of heat and light. One of the bodies, as hydrogen or sulphur, is termed the burning or combustible body, and the oxygen is said to be the supporter of combustion; but this language, although convenient for common use, is incorrect as a scientific expression; for oxygen may be burned in a vessel of hydrogen, as well as hydrogen may be burned in a vessel of oxygen gas, the one and the other being equally active in the process, and being related to each other in every way alike. In combustion, as, indeed, in all cases of combination, no particle of matter becomes lost or annihilated; it assumes new forms, in general gaseous and invisible to the eye of popular observation, but easily collected, weighed, and analyzed by the means that chemistry possesses. The solid coal or wood which burns to ashes, changes but its external aspect; mixing with the general mass of air under the form of carbonic acid gas and watery vapour, its elements become the food of living plants, which in their turn, cut down or fossilized, form to succeeding ages the stores of light and warmth such as we now enjoy.

There are but few bodies endowed with so great an affinity for oxygen as to enter into combustion at ordinary temperatures by contact with it. If they do combine at ordinary temperatures with oxygen, the products are not those which combustion would tend to generate, but a distinct class of substances, containing a smaller proportion of oxygen combined. Thus nitric oxide gas combines with oxygen, even when quite cold, forming red fumes of nitrous acid gas, which is an inferior degree of oxidation. Phosphorus, when burning at common temperatures, emits but little light, and forms phosphorous acid; if it be heated, it bursts into brilliant flame, and forms phosphoric acid, which contains

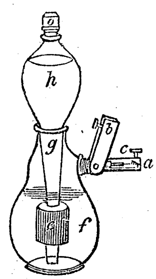
$\frac{2}{5}$ths more oxygen. Potassium combines at common temperature with oxygen, forming potash; but when heated it burns with flame, and combines with three times as much oxygen. In the complete combustion of organic matters, the products are always water and carbonic acid. Thus, woody fibre, which is C.H.O., combines with 2O. to form $C.O_2$ and H.O.; and alcohol, which is $C_2H_3O.$, combines with 6O. to form $2(C.O_2)$ and 3(H.O.). But at common temperatures the slow oxidizement of woody fibre produces the black vegetable mould, a form of ulmine, the C.H.O. taking O. to form $C.H.O_2$. At common temperatures alcohol becomes acetic acid, the $C_2H_3O.$ combining with 2O. to form $C_2H_2O_2$ and H.O. The pyroxylic spirit at common temperatures becomes, by slow combustion, formic acid, $C_2H_4O_2$ taking O_4 to form $C_2H_2O_4$ and 2(H.O.).

This slow combustion produces heat, although so much less than is evolved by the more rapid process that it may easily be overlooked. But if a number of sticks of phosphorus be laid together and allowed to oxidize, they will warm each other so much as to melt and burst into vivid flame. The oils and tallow, if there be a large surface exposed to the air, as when cotton or linen rags im bibed in oil lie in a heap, combine so rapidly with oxygen as to form a sort of resin, that by the heat evolved the mass will be set on fire; and hence the origin of those spontaneous fires, so called, which consumed the naval arsenal at St. Petersburgh, and, in many cases, cotton-mills in England. To this cause also may be ascribed the light which issues from points in the surface of a marsh or bog, and the luminous appearance which fish assumes when decomposition has just commenced. The energy of this slow combustion may be much increased by heat applied below the point which produces rapid action: thus tallow, when heated below redness, burns with a pale lambent flame, invisible in daylight, but still so marked that, if it be plunged into a vessel of oxygen, the whole mass bursts into brilliant combustion, forming then the ultimate products, water and carbonic acid.

On this fact of the increased energy in the process of slow combustion produced by a heat below that at which the body is inflamed, is founded the construction of the lamp without flame, or the *aphlogistic lamp*. If a wine-glass be taken, and rinsed inside with strong alcohol or ether, and then a coil of fine platina wire, or a ball of spongy platina heated to redness, be suspended in the middle of the glass, it will remain red until all the alcohol or ether has been exhausted. The glass becomes filled with a mixture of air and inflammable vapour, which, by the influence of the heated platina, is enabled to combine, and form acetic and formic acids. By this combination heat is evolved, which prevents the cooling of the wire or ball, and thus, as long as any combustible material remains, the platina is kept ignited. The platina ball or wire may also be (and in practice generally is) fixed over the wick of a spirit-lamp, and the lamp having been ignited, is blown out as soon as the platina has become red, which then continues to glow until the lamp has been emptied of the spirit, the latter ascending through the capillary wick, and forming over its top a little explosive atmosphere, in which the ball of platina is immersed and works.

This property of platina appears to depend on the power which it possesses of attracting to its surface in a condensed form a layer of particles of whatever gaseous mixture it is immersed in. Hence, if its surface is in the slightest degree soiled, it ceases to exert this action; and by increasing the surface, its energy may be augmented in a remarkable degree. The form in which it is most powerful is that of the slightly coherent spongy mass, obtained by reducing at a full red heat the ammonia chloride of platinum; if a ball of the metal so prepared be plunged into a vessel of oxygen and hydrogen, mixed in suitable proportions to form water, the gases instantly explode; for the oxygen and hydrogen, being absorbed by the spongy platina, are brought into intimate contact upon its surface, and unite, evolving so much heat as to raise the temperature of the platina ball to redness, and thereby inflame the remaining gas. The action of the spongy platina may be weakened by mixing it with some pipe-clay, or using, as in the aphlogistic lamp, the platina in the form of plate or wire. In this way all combustible gases may be caused to combine gradually with oxygen, but they require different temperatures, and the action is modified by the presence of other gases in a manner which is often taken advantage of in gaseous analysis.

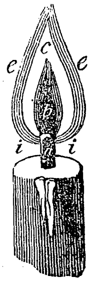
The most remarkable application of this property is to procure instantaneous light by means of the hydrogen gas lamp. A vessel, *f*, contains dilute sulphuric acid, into which the tube of the vessel *g h* dips nearly to the bottom, having attached a piece of ordinary zinc, *e*. The vessels being ground air-tight where they fit to one another, when the stopcock *b* is closed, and the acid acts on the zinc, the hydrogen evolved cannot escape, and, pressing on the liquid in *f*, forces it up into *h*, until the acid falling below the level of the zinc, the action ceases. To the stopcock *b* is attached a jet, *c*, in front of which is fixed a ball of spongy platina, *a*, which, being in the air, has always condensed in its pores a quantity of oxygen gas; on opening the stop-cock, the hydrogen, issuing from the jet, strikes upon the platinum, and combining with the oxygen, heats the ball so highly that it inflames the jet of gas, and thus affords a flame at which any other substance may be lighted. This lamp has assumed a variety of forms, of which the above is that which best shows its principle. All bodies possess this property to a slight extent, particularly when hot; but in none is it active enough to be usefully applied, except in platinum.



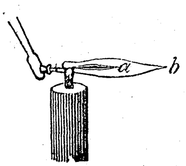
The temperatures at which bodies enter into rapid combustion are very various; thus phosphorus inflames at a temperature of 120° F., and sulphur at 300° F. Phosphuretted hydrogen gas inflames at all ordinary temperatures, while hydrogen requires a dull red, and carburetted hydrogen a bright red heat before they will take fire. The inflammability of phosphorus has been shown by Graham to be affected by the presence of small quantities of various substances in a very curious manner; thus phosphorus may be sublimed in air saturated with vapour of oil of turpentine, without any tendency to combustion, or combination with oxygen, being evinced.

Combustion occurs only at the point where the two substances

which enter into union are in contact. Thus, in an ordinary flame, the true combustion is limited to a thin sheet, the inside of which is totally dark, and occupied by the combustible material of the burning body in a state of gas. This is easily shown by holding over the flame of a candle or a spirit-lamp a piece of wire gauze: the burning sheet is marked by a ring of light, but the interior is dark, although full of inflammable vapour, which passes through uninflamed, and may be ignited on the opposite side of the gauze. In the flame of an ordinary candle, *a*, four distinct portions may be observed, having totally distinct constitutions; at the base of the flame, *i i*, a pale, blue-coloured light is emitted, for there the air is in excess, and the combustion is at once complete; higher up, from *i i* to *c*, the combustible material is in excess, and the most brilliant light is produced by the active combination; this portion is surrounded by a sheet of much paler and yellower light, *e e*, which is observable particularly at the sides of the flame, while the inside of the flame, *b*, remains completely black, and is occupied only by vapour incapable of burning from having no access to the external air. The light emitted arises also from the circumstances of the combination; the temperature of flame is in all cases exceedingly high, although often but little luminous, for it is found that a current of air hot enough to brilliantly ignite a solid body, is itself not at all incandescent. Hence, in all cases where bright light is produced in combustion, one of the bodies engaged must be solid, and the light is really derived from its becoming ignited. Thus hydrogen and sulphur give, in burning, very little light, because the one is a gas, and the other, when burning, is in the state of vapour, and the products of combustion are, when formed, in both cases gaseous. Phosphorus, when it, in burning, forms a volatile body, gives but little light, but when it forms a fixed product, is one of the most brilliant instances of combustion. Iron and zinc, which form solid oxides, burn with great light, and carbon, although forming a gas, being itself solid, produces light also. In the case of a candle, the source of light is to be found in the decomposition which the inflammable vapour inside of the flame undergoes from the high temperature to which it is subjected; one half of its carbon is deposited in the solid form, forming smoke, and it is this smoke which, becoming ignited, constitutes the great source of light. A body which could not form smoke, could not give out much light in burning. The separation of this carbon (soot) in the flame may easily be shown by placing over the flame of the candle a sheet of wire gauze: below the middle of the luminous space the flame becomes dull, and the carbon, which in burning should have rendered it brilliant, passes as smoke through the gauze, and may be inflamed above; when the supply of air is insufficient, this smoke is not completely burned, and a corresponding quantity of heating and lighting material is lost; and as it carries off with it a great quantity of the heat already formed, it actually cools the flame. When, therefore, a high temperature, or a clear flame without smoke is required, all the carbon must be consumed. This is effected by a variety of contrivances: in the burner of the Argand lamp or gas



jet, a current of air is established through the centre of the flame, and thus the combustion of the inflammable vapour much accelerated; in the flame of the blowpipe the same effect is produced by the current of air from the bellows or the mouth; and on a large scale by the numerous ways of burning smoke, so necessary in factories situated in large cities. In the employment of the blowpipe, the constitution of the flame is of great importance; for according



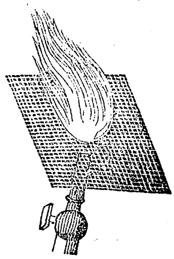
as the body to be heated is placed at *b*, where the oxygen of the air preponderates, or between *a* and *b*, where it is immersed in an atmosphere of inflammable material, the most opposite effects of violent oxidation, and of reduction from the state of oxide, may be produced. Thus a glass of copper becomes green at *b*, and red from *a* to *b*; a glass of manganese is rendered purple at *b*, but colourless from *a* to *b*; there being few bodies whose relations to the blowpipe can be completely known without a comparison of the effect of the oxidizing and reducing flames.

During combustion, the heat evolved is at first absorbed by the body which is then produced; but it is afterward distributed through the mass of all neighbouring bodies in proportion to their conducting powers. It is easy to calculate the temperature to which the product of the combustion is in the first place raised. Thus eight parts of oxygen unite with one part of hydrogen by weight to form nine of water. If watery vapour had the same capacity for heat as water, the temperature of the vapour produced should be, since one part of oxygen heats twenty-nine parts of water, 180 degrees $=\frac{8}{9}(29\times180)=4640$ above the freezing point; but the capacity of watery vapour in equal weight is only 0·847, and therefore it is more easily heated in that proportion than liquid water; hence the temperature really produced is $=4640\times0{\cdot}847$, or 5478 above the freezing point of water. If, however, in place of pure oxygen, atmospheric air had been made use of, then 23·1 parts of oxygen are mixed therein with 76·9 parts of nitrogen, which must be heated to the same temperature with the watery vapour, and, of course, at its expense. The capacity of nitrogen gas for heat is 0·2865, one third that of watery vapour; but in the air which is necessary to form nine parts of water, there are 26·8, or almost exactly three times as much nitrogen, so that precisely one half of the quantity of heat produced is absorbed by the nitrogen, and the temperature of the mixture rises only to 2739° above the freezing point.

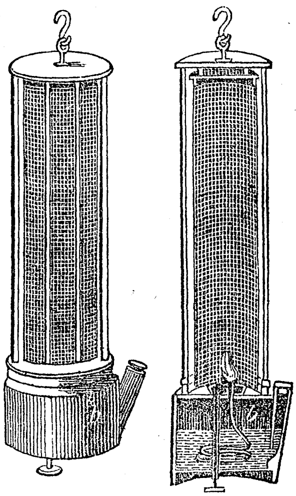
Such being the temperatures produced by hydrogen gas in burning in oxygen and in atmospheric air, it is easy to understand why we can by its power fuse those substances which resist almost every other means. The melting point of cast iron is 2786°, that is, almost exactly the same as that produced by hydrogen burning in the open air; but the temperature of 5478°, given by hydrogen burning in oxygen, is very nearly double that, and passes, therefore, far beyond the melting point of platinum, and exceeds the heat of all our other artificial fires; it is only in the discharge of the galvanic battery, or in the solar rays concentrated by a lens, that the heating effects of burning hydrogen and oxygen can be equalled. If the nitrogen had been present in a quantity ten times as great, it would have absorbed $\frac{10}{11}$ of the amount of heat evolved, and hence the resulting temperature should be only about 500°. Such a mixture, therefore, could not explode at all, for the first little portion which might be burned could not produce the necessary temperature for communicating the combustion to the mass. In this manner, the combustibility of gaseous mixtures may be destroyed by mixing them with other gases in such quantities as may cool them below the temperatures at which explosion can take place. One volume of a mixture of oxygen and hydrogen is prevented from exploding by the presence of nine volumes of hydrogen, six volumes of nitrogen, one of olefiant gas, two of ammonia, three of carbonic acid; but with eight volumes of hydrogen, or five volumes of nitrogen, explosion may occur.

The greater density of solid bodies, and the greater rapidity with which they are capable of conducting away the heat which they re

ceive, enables them, in a still more remarkable degree, to reduce the temperature of flame, and, consequently, to extinguish it. Thus, if a piece of metallic gauze be held over a jet of ignited coal gas, the flame will be arrested at the lower surface of the gauze; and although the gas and air may pass through, forming an explosive mixture, yet no inflammation can be propagated; and if the mixture of air and gas be allowed to pass through the metallic gauze, and then ignited at its upper surface, it will burn there; but, although the space between the jet and gauze be occupied by inflammable material, the flame cannot pass down, the metallic tissue conducting away the heat so rapidly as to prevent the temperature from rising to the necessary degree. Another and a very striking form of this experiment is to lay on the metallic gauze a piece of camphor, and to hold it over a lamp; the camphor will melt and vaporize, but as it melts it will in part filter through the gauze; this portion takes fire, and a sheet of smoky flame covers the lower surface; but above, the camphor in vapour mixes with the air without inflaming.



The application of this principle to the construction of the safety-lamp for mines, constitutes one of the most beautiful instances of the advantages which may practically flow from what, superficially considered, might appear a mere abstract principle in science. The fire-damp, or light carburetted hydrogen, which, issuing from the minute fissures in the excavations of a coal-mine, is diffused through the air introduced for the purposes of ventilation, often forms an explosive mixture, which, being set on fire by accident or negligence, detonates with awful violence, and destroys all living beings which may at the time be in the mine. This gas is one of the least easily inflammable, and hence, most fortunately for humanity, one to which the principle of cooling orifices may be most successfully applied. The candle or lamp, *b*, by which light is to be obtained for working in the mine, is surrounded by a cylinder of wire gauze, of about 1500 orifices in the square inch. Inside of this the inflammable mixture may explode, but the flame cannot pass out; the combustion cannot be communicated to the general mass of external air, and thus the miner, guided by the never-failing indications of his safety-lamp, passes along through galleries under ground, where the emission of a spark would cause destruction, and measures, by the appearance of the lamp, the actual condition of the air he breathes, the phenomena of the flame indicating also its fitness for respiration. If the air be pure, the lamp burns clear, as in the upper air; if some fire-damp be present,



the lamp shows much less light, the flame becomes red and smoky; if the noxious impregnation be still increased, the flame of the lamp itself becomes extinguished, and the cylinder of metallic gauze is filled by a sheet of lurid flame; the miner being then enveloped by an atmosphere fully explosive, and even fatal to life if it be long respired. If he proceed still farther, all flame is lost; for, as the fire-damp then predominates, there is produced, from deficiency of oxygen, only a slow invisible combustion; but even this is made, by the sublime genius of its inventor, Davy, to give the miner the last warning to return to safer regions: a sheet of thin platina, being coiled up and hung over the wick of the lamp, becomes ignited, as in the aphlogistic lamp, and continues to emit a faint, but most use ful beacon glow, until an atmosphere is obtained where there is oxygen enough to support a rapid combustion, or until a place is reached so destitute of oxygen that no combustion whatsoever can take place.

The determination of the quantity of heat produced during the combustion of a given quantity of combustible substance is a problem of great importance in the arts, as on it depends the economic value of all varieties of fuel. The plan generally followed has been to burn the substances by means of the smallest quantity of air which is sufficient, in a vessel surrounded, as far as possible, with water. If it be found that the burning of a pound of wood heats 37 pounds of water from 32° to 212°, no idea can be thereby formed of the quantity of heat evolved; but if, in another trial, it be found that the burning of a pound of charcoal raises the temperature of 74 pounds of water through the same range, it follows that the charcoal had double the calorific power of the wood. True relative numbers can thus be obtained, although they have independently no positive signification. The results obtained in this manner have been exceedingly discordant; but, by the late researches of Des pretz and of Bull, which appear to have been conducted with more attention to accuracy than former ones, a very interesting rule has been obtained: it is, that in all cases of combustion the quantity of heat evolved is proportional to the quantity of oxygen which enters into combination. Thus Despretz found

1 lb. of oxygen,	uniting	with hydrogen,	heats from 32°	to 212°,	$29\frac{1}{2}$	lbs. of water
"	"	" charcoal,	"	"	29	"
"	"	" alcohol,	"	"	28	"
"	"	" ether,	"	"	$28\frac{1}{2}$	"

This rule, however, must be liable to some very curious changes; for one pound of oxygen, in combining with iron, could heat, by Despretz's experiments, 53 pounds of water, or almost exactly twice as much as in the former list, and with tin and zinc the same double proportion held. With phosphorus a singular peculiarity was observed, which, when the subject comes to be more fully studied, may throw some light upon the former differences. When phosphorus burns slowly, so as to form phosphorous acid, it heats, in combining with a pound of oxygen, 28 pounds of water; but when it burns brilliantly and forms phosphoric acid, the heat evolved is doubled, and becomes the same as that produced with iron, tin, or zinc. As a suggestion, I would remark, that in the cases where the smaller proportion of heat is evolved, the products of combustion are all volatile, and where the larger proportion is produced, the products are fixed and solid; even in the case of phosphorus, when it combines, producing least heat, it forms a volatile product, but one which resists a full red heat in the case where the combination has been complete.

Hess has lately pointed out a relation between the amount of chemical action

and the quantity of heat evolved, which may, when examined in a greater number of cases, lead to very important conclusions. He has found that sulphuric acid, in combining with any base, generates in all cases the same quantity of heat; the rise of temperature is, of course, greatest when the acid and base are both in an uncombined condition, as where vapour of anhydrous sulphuric acid produces, by contact with dry barytes, brilliant ignition; but, although the barytes generates, by contact with dilute sulphuric acid, much less heat, yet, if the two quantities evolved, first by mixing the strong acid with water, and then the dilute acid with the base, be added together, the sum appears, from a great number of experiments, to be constant; thus, diluting oil of vitriol with water, and neutralizing it, so diluted, with ammonia, Hess found the heat in each case to be,

	With Ammonia.	With Water.	Sum.
Oil of vitriol	595·8		595·8
First dilution	518·9	77·8	596·7
Second dilution	480 5	116·7	597.2

Connecting these results with those of Despretz, just given, for the bodies which unite with oxygen, it would appear likely that the quantity of heat evolved in chemical combination may be connected with the equivalent number and the electrical condition of the substances by a definite law, which farther investigation may disclose.

At all periods in the history of chemistry, the explanation of the phenomena of combustion was that for which the general theory of the science was constructed; and, accordingly, we find that every period of its progress has been marked by the views adopted to account for the heat and light so evolved. The coarse and unphilosophical ideas of the existence of inflammability which prevailed before Lavoisier's time, do not require notice; but the theory which he proposed, although not now received, is yet, like all his works, of so much interest and importance, that it would be improper to pass it over.

When Lavoisier lived, the minds of philosophers were fixed in the opinion that heat and light were positively existing substances, which might enter into combination, or be disengaged from combinations in which they had previously been engaged, just as lead, or oxygen, or any other of the ordinary bodies we operate upon in our experiments. Gases were believed to be compounds of the true solid body with light and heat; and hence, when oxygen gas combined with iron or with phosphorus, and assumed the solid form, the light and heat with which the real oxygen had previously united were set free. Hydrogen and oxygen gases, in combining to form liquid water, underwent the greatest condensation, and by their union, therefore, the greatest heat was evolved; and in all such cases where a gas became a liquid or a solid, this theory was fully competent to explain the facts. However, in very many cases it failed completely; thus, by the union of carbon with oxygen, so far from a gas becoming solid and so evolving a heat, a solid becomes a gas, and should produce an equivalent degree of cold. Lavoisier here brought in to his aid the relative specific heats of the gases before and after union; thus, if the carbonic acid formed by burning carbon in oxygen gas had a much less specific heat than oxygen, there might be evolved a quantity of heat in the same way as it occurs with water and sulphuric acid; but this is not the fact; on the contrary, the carbonic acid has a specific heat greater than that of the oxygen gas it was formed from, in the proportion of 1195 to 808; and hence, on Lavoisier's views, an intense degree of cold should be produced in the combustion of charcoal, as well by the latent heat which the solid should absorb in becoming gaseous, as by the increased specific heat of the gas so formed. This example is sufficient to show the way in which Lavoisier's theory became inapplicable to the wants of science.

Dr. Thompson has recently endeavoured to account for the heat evolved in chemical combination by an application of the law of Dulong regarding specific heats (described page 66). Every molecule of a simple body being supposed provided with the same quantity of heat, he suggests that, when a number of them combine together, the heat of one or more is expelled, and thus produces the rise of temperature. Thus, considering oil of vitriol to contain seven combining equivalents, two of hydrogen, four of oxygen, and one of sulphur, and that the specific heat of all of these is the same, 3·1, as results from Dulong's law if it be supposed rigidly exact, the specific heat of oil of vitriol should be $\frac{3{\cdot}1 \times 7}{49{\cdot}1} = 0{\cdot}442$, 49·1 being the

equivalent number of oil of vitriol; but the specific heat found by experiment is only 0·352; so that exactly one fifth of the total quantity of heat has been lost by the act of combination, and may hence be supposed to have caused the phenomena of combustion.

In the extension of this principle a little farther than Dr. Thompson appears to have contemplated its application, some coincidences, with results already known, are found, which give it an aspect of considerable theoretic interest. Thus we may consider certain metallic oxides as consisting of an equivalent of each constituent, and hence their proper specific heat should be, if none were lost by combination, $3·1 \times 2 = 6·2$; but the specific heat of the compound molecule is experimentally found to be 5·4, and thus that 0·8 of heat had been lost, producing the phenomena of combustion in combination. In this manner we can understand why Despretz found that a certain quantity of oxygen evolves the same quantity of heat in combining with very many bodies. If we examine the sulphates noticed, p. 67, in relation to the same principle, we find that as there are in each six molecules, the specific heat should be $18·6 = 3·1 \times 6$; but it is found to be but two thirds of that, 12·4. Now if here, as in the oxides, the combustible material retains its heat, and it is from the oxygen that the portion set free is taken, the experimental result arises from the heat of each oxygen molecule being reduced by 1·6, and hence that when oxygen forms a salt with sulphur and a metal, the heat evolved is double that produced in simple oxidation. The fact of the same quantity of oxygen giving double the amount of heat when it converts phosphorus into phosphoric acid, compared with what is evolved when it forms only phosphorous acid, may have its origin in an analogous condition.

In the case of the carbonates, another form of the principle becomes manifest; but on this view it is necessary to consider carbonic acid as containing five molecules, one of carbon and four of oxygen, and as uniting with two molecules of a metallic oxide. The carbon and metal burn each in half of the quantity of oxygen with which they ultimately unite, and, like phosphorus, separate from that oxygen only the smaller quantity which it can lose when entering into combination; the carbonic acid and suboxide then unite with the residue of oxygen, and from it separate the larger portion of heat as occurs when phosphoric acid is produced. The resulting specific heat for a carbonate is therefore $9·3 + 6·9 + 5 = 20·7$; or, reduced to the equivalent number used in p. 67, it is 10·35, the experimental number being 10·4.

The results in these three cases may be shown in the form of the following table, in which the first column contains the equivalent molecule of the body, M. denoting the equivalent of a metal; the second column contains the specific heats calculated on the supposition that there is none lost in combining; the third, the calculation by which the fourth column of true calculated specific heats is obtained; and the fifth, the specific heats that have been found by experiment.

1.	2.	3.	4.	5.
M. O.	6·2	$3·1 + 2·3$	5.4	5·4
M. O_4S.	18·6	$(2 \times 3·1) + (4 \times 1·5)$	12·2	12·4
M_2O_6C.	27·9	$(3 \times 31) + (3 \times 2·3) + 3 \times 1·5)$	20.7	20·8

The coincidences refer only to the bodies already selected, p. 67, as examples of simplicity in the relation of their specific heats, and certainly do not exist in a great number of other cases in which I have sought for them; they may therefore be accidental; but there is yet so much likelihood of some physical law of the kind being to be discovered, that everything that may assist in its detection is of importance.

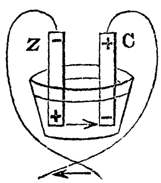
Laying aside altogether the attempt at deducing the phenomena of combustion from any change in the amount of latent or of specific heat in the bodies which enter into combination, it remains only to be admitted as a general and independent principle that chemical combination is a source of heat and light. It is, however, impossible to arrest inquiry at that point, and, accordingly, the speculations of philosophers have been directed in seeking a cause for the phenomena of combustion to the disengagement of electricity, which accompanies all manifestations of chemical action, and have endeavoured to identify the light and heat emanating from a burning body with that which is produced by the separation or combination of the electric fluids. The evidence in favour of this view will be best described among the relations of electricity to affinity.

CHAPTER VIII.

OF THE INFLUENCE OF ELECTRICITY ON CHEMICAL AFFINITY.

It has been already shown, that in the production of galvanic or hydro-electric currents, there always occurs between the liquid and solid elements of the circle a degree of chemical action, to which the quantity of electricity generated is exactly proportional in amount, and that no current, such as was there described, can be generated without, by the chemical action of the more oxidizable metal, the liquid being decomposed, and some one element of it expelled, in place of which a corresponding quantity of zinc may be substituted. I did not then attempt to discuss the question of whether the chemical action in the battery be the cause or the effect of the current of electricity which arises, as that can be best done when the action of the current, no matter from what source it may have been derived, upon chemical substances, similar to those that are used as exciting liquids in the galvanic battery, has been described.

If the wires belonging to the plates Z C, of the simple circuit in the figure, be brought into communication by means of a cup of water, the current passes, and it is found that at the terminations of the wires bubbles of gas form in considerable number, which, when collected, are found to be, from the wire in connexion with the copper plate, oxygen gas, and hydrogen gas from the wire which is attached to the plate of zinc. If the conducting liquid had been muriatic acid, hydrogen would have been evolved as gas at the zinc extremity, and chlorine liberated upon the wire of the copper plate, though from its solubility in the liquid it would not be disengaged as gas.



If a solution of iodide of potassium had been employed, iodine would appear upon the copper side, and potassium should be set free upon the zinc wire; but by the action of the water, the metal is instantly converted into potash, and hydrogen set free.

It is not necessary that such bodies should be in solution, for this only serves to give to their particles the freedom of motion, which may allow their elements to separate. If chloride of lead melted in a cup be used to complete the voltaic circuit, chlorine is evolved upon the +, and lead upon the — wire; with oxide of lead (litharge), the evolution of lead at the —, and of oxygen upon the + extremity of the wires, occurs similarly; protochloride of tin, iodide of lead, chloride of silver, all act in the same way.

In place of bodies consisting of two elements, such as those above described, we may employ in solution, or in a fused state, secondary compounds, consisting of an acid and a base. If the current of electricity pass through a solution of sulphate of soda, the sulphuric acid appears upon the +, and the alkali upon the — wire. With sulphate of magnesia, the earth passes to the negative, and the acid to the positive extremity of the liquid circuit; in these cases water

is also decomposed, of which the hydrogen accompanies the base, and the oxygen the acid; but, on using a salt of lead, of silver, or of copper, the metallic oxide is reduced by the action of the nascent hydrogen, or, at least, it may be so expressed, and the metal is deposited in crystals upon the — wire, while the acid and the oxygen are evolved together upon the extremity of the positive conductor.

The affinity which held together these bodies in combination is superseded during the passage of the electric current. The elements previously united appear to repel each other, and to be at the same time attracted by the excited terminations of the metallic wires, by which the battery is placed in connexion with the substance to be decomposed.

The simplest mode of accounting for these phenomena is to say that water is decomposed, because the oxygen is attracted more powerfully by the positive pole of the galvanic battery than by the hydrogen with which it had previously been associated, while this last is more powerfully attracted by the negative pole than by the oxygen. The elementary bodies separate, therefore, from each other; but, not being capable of entering into combination with the substance of the poles, they are evolved as gas. This explanation may be applied to all such cases. Oxygen, chlorine, iodine, sulphur, as well as the various acids, are attracted by the positively electric pole, while hydrogen, potassium, sodium, copper, silver, lead, and the various bases, are attracted to the negative pole of the battery. But one force cannot completely supersede another, as electricity here supersedes affinity, unless it be of the same kind, or, at least, closely resembling it in nature. What, then, is the relation between the chemical force which had kept the elements united, and the electrical force which makes them separate? The cause was easily found: they are identical. The oxygen and hydrogen united originally from being in opposite electrical states, and they are forced to separate from being subjected to the action of still more powerful attractions; the decomposition of water by the voltaic current becoming thus a case of double decomposition, in which the original electricities of the two simple bodies were the quiescent, and the excitation of the opposite poles of the battery were the divellent forces.

Chemical substances were thus considered to have affinities for each other, from being in opposite electric states, and the peculiar play of affinity of each body depended on which electricity it was naturally excited by when in combination; those bodies which are attracted by the positive pole of the battery being necessarily in the negative condition, and *vice versa*. Thus, all substances may be divided into two classes, those being termed electro-negative which are evolved at the copper pole of a simple, or at the zinc pole of a compound circle, and those which appear at the opposite pole being termed electro-positive. The simple bodies thus classified are ranged as in the following list:

Electro-negative.			Electro-positive.
Oxygen.	Mercury.	Palladium.	Potassium.
Fluorine.	Chrome.	Silver.	Sodium.
Chlorine.	Vanadium.	Copper	Lithium.
Bromine.	Iridium.	Lead.	Barium.
Iodine.	Rhodium.	Tin.	Strontium.
Sulphur.	Uranium.	Bismuth.	Calcium.
Selenium.	Osmium.	Cobalt.	Magnesium.
Tellurium.	Platinum.	Nickel.	Glucinum.
Nitrogen.	Titanium.	Iron.	Yttrium.
Phosphorus.	Gold.	Manganese.	Thorium.
Arsenic.	Molybdenum.	Cadmium.	Aluminum.
Antimony.	Tungsten.	Zinc.	Zirconium.
Silicon.	Columbium.	Hydrogen.	Lanthanum.
Boron.		Carbon.	Cerium.

The most powerfully negative bodies are placed in the first, and those most powerfully positive in the fourth column, these being connected by the intermediate columns in the order marked by the brackets and arrows. Any substance in the list is positive with regard to any other towards which the arrow points, and negative in relation to any from which the arrow is directed. Thus hydrogen is negative to all in the fourth, but positive to all in the three preceding columns, and so on. These positions should also indicate the relative affinities of the simple bodies towards each other; but, in interpreting such arrangements, it must be recollected that the order of affinities may be totally changed by heat or by cohesion, and that the electrical order may be completely different, according to the nature of the exciting liquid, as in the table, p. 129.

Two bodies in combination are therefore like two pith balls which mutually adhere, but of which the attraction is permanent from their electricities not being discharged. How do these bodies acquire those oppositely excited states? and why, if their condition resembles that of ordinary electricity, do they remain combined, when their opposite fluids might unite, and neutralization being produced, all combination cease?

These two questions have not yet been answered. Several times their explanation has been attempted; and thus the electro-chemical theories of Davy, Ampere, and Berzelius have been proposed. I shall briefly notice the leading features of these before proceeding to discuss the remarkable advance recently made in our ideas of the electro-chemical relations of bodies by Faraday and Graham.

The theory of Davy was based upon the principle that bodies in their ordinary uncombined condition do not contain free electricity, but that by contact they become excited. Thus a disk of sulphur touched to a disk of copper becomes negative, and the copper positive; its charge increases in intensity on applying heat, until, at a certain temperature, the tension of the electricities becomes so great that they suddenly recombine, carrying with them the molecules of the sulphur and copper which thus enter into union, and producing the evolution of light and heat by which the chemical action is accompanied. The sulphuret of copper, when formed, is no longer electric; it remains permanent in virtue of a force which Davy does not strictly define, but which he appears to have considered an intimate cohesion between the particles which had been closely approximated by their electrical attractions; and when, by an electric current, the molecules of copper and sulphur are brought into the reverse state to that which favoured their combination, they separate. This view supposes, therefore, the electrical excitation to be only momentary, during the act of combination and during the moment of disunion; before and after, all is neutral. To all phenomena of decomposition this theory suffices, but it is vitally deficient in the principle upon which it is based. It has been since

completely proved that it is not the contact which evolves electricity, but the chemical action; and also, on Davy's views, the electrical disturbance only suffices to account for the secondary phenomena of union, the light and heat, leaving the act of combination to be ascribed to a different and independent force of affinity or cohesion.

A more complete theory was proposed by Ampere, whose philosophical views in magnetism and other sciences have been found so singularly in accordance with experiment. He proposed to consider that each substance in nature is endowed with a definite amount of one or of the other electricity, and is thus naturally and invariably electro-positive or electro-negative, and stands higher or lower in the list of bodies, according to the intensity of the charge. Such an excited body he considered to attract round its mass an atmosphere of electricity of the opposite kind, and corresponding in intensity. Now, on bringing into contact an electro-positive and an electro-negative body, their atmospheres unite, and produce the heat and light resulting from their chemical action on each other; but the bodies themselves must remain permanently combined, as each retains its own excitement, and they hence attract without cessation. When one body is exactly as negative as the other is positive, the resulting compound cannot manifest any signs of electro-chemical activity; but if the charge of the negative body be more powerful than that of the positive element, the resulting compound will be negatively excited to the amount of the difference between the two; if the proportions be reversed, the new body formed will be positive in the same degree; and such compound electro-negative and electro-positive bodies, being acids and bases, attract each other, and unite to form neutral salts.

All that was difficult to comprehend upon the theory of Davy is here beautifully explained. The light and heat of combination are produced by the atmospheres of electricity; the permanence of combination by the invariable excitation of the molecules. The gradually diminishing intensity of charge, according as the bodies formed become more complex, necessarily follows; but the assumption that any one body is naturally and invariably positive or negative, is contradicted by the history of almost all the simple substances.

Thus, if sulphur or arsenic be heated in oxygen gas, they burn, and the combination is effected with all the phenomena of intense action, the resulting compounds being acid and electro-negative. The sulphur and arsenic are thus shown to have been feebly positive bodies. But if sulphur or arsenic be heated with potassium, there is similarly combustion, showing that chemical combination has taken place; and as potassium is the most positive body in the series, the sulphur and arsenic must be the negative elements of the compounds. Sulphur and arsenic are therefore at one time positive, and at another negative. There is, indeed, no substance known which can be said to be invariably negative or positive. Nor can the amount of negative or positive excitement be in any case looked upon as constant, for oxygen is often found to be less negative than chlorine, and potassium to be less positive than iron or than carbon; and hence, if electrical forces be considered as representing affinitary power, they must be capable of the same fluctuations in intensity.

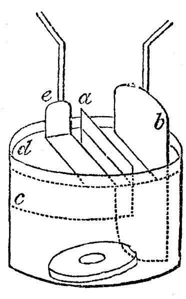
It was for the purpose of bringing Ampere's theory into harmony with the changes of chemical decomposition, that Berzelius proposed the modification of it which now remains to be described. He suggested that each body should be looked upon as containing the two electricities, but that the one might be more powerfully developed than the other, as in a magnet one pole may be stronger than the other; also, from the analogy of certain bodies, which were supposed to admit the passage of one electricity rather than the other, he imagined that a body thus excited with the two fluids might discharge the one and yet retain the other. Thus oxygen possesses high negative and feeble positive excitation; hydrogen an intense positive, but a feeble negative charge. When these bodies combine, the phenomena of combustion follow from the union of the positive fluid of the oxygen with the negative of the hydrogen, and the more intense and more permanent charges retain the bodies in combination. To account in this way for certain bodies being at one time electro-negative and at another electro-positive, Berzelius considers that, when potassium is brought into contact with sulphur, the naturally feeble negativity of the latter is heightened by induction, while, if the sulphur be acted on by oxygen, it is its positive charge that is increased; and thus any substance near the middle of the electro-chemical series may become positive or negative, according as it combines with a body situated nearer to the negative or positive extremity.

This view might explain most chemical phenomena; but it is, like Davy's theory, founded on physical principles which cannot be considered sound. Thus, although the effect of one pole of a magnet may be weaker than another, that only happens where the action is complicated by the existence of more poles than two; and in all cases the amount of north and south magnetism present is exactly equal. Also, the fact of the existence of bodies which conduct the one better than the other electricity, is now abandoned by all sound reasoners, and cannot be looked upon as even in any degree probable in theory. Indeed, all views like those of Berzelius and Ampere, which are founded on the existence of different degrees of electrical excitement, which represent the different powers of affinity by which chemical substances combine, must be now abandoned; for it has been proved by Faraday that a molecule of oxygen, in uniting with hydrogen to form water, or with zinc to form its oxide, a molecule of iodine or chlorine uniting with lead, with tin, with silver, or with potassium, bodies so far separated in the electro-chemical scale founded on their reactions, evolve in uniting the same quantity of electricity, and require for their separation, when combined, the same amount of current derived from another source.

Before more definite and correct ideas of the electrical relations of chemical substances can be obtained, it is necessary to study somewhat more in detail the chemical phenomena which occur in the galvanic battery, which, for simplicity, shall be considered as a simple circle, and in the liquid through which the circuit is completed; the former is generally termed the generating, and the latter the decomposing cell.

The decompositions hitherto described have been considered as resulting from the attractive and repulsive forces of the extremities of the wires, on which the charge of the battery was supposed to be collected. But, when the circuit is completed, no such accumulation can exist; once the current passes, it is everywhere present in equal quantity and of uniform tension; and such forces of attraction and repulsion, acting upon molecules already electrically excited, were only imagined for the foundation of the imperfect theories already noticed, and, when impartially examined, are found to have no real existence. It is also fatal to the idea of attractive forces exercised by the poles, that the substances evolved upon their surface do not necessarily combine with them; thus, if one platina pole have such attraction for oxygen as to separate from the hydrogen it had been united with, it is unreasonable that it should lose, suddenly and completely, this power, and allow the oxygen totally to escape; the other platina pole behaving similarly to the hydrogen.

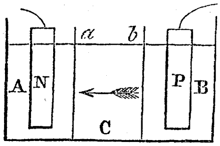
Faraday has definitely shown that the disengagement of the substances, which are separated from each other by the current, takes place in all cases at the bounding surfaces of the body decomposed; and that where they are evolved on the metallic conducting wires, it is only because those are the limits of the decomposing fluid. The proofs of this principle are numerous and simple: thus, in a glass basin, a partition of mica, *a*, is cemented so as to be completely water tight, and extending half way to the bottom; a strong solution of sulphate of magnesia is poured in until it rises a little above the edge of the partition, and then distilled water poured in on the side *c*, *d*, with such precaution that it shall not mix with the saline solution, but shall float on it, the surface separating the two



liquids remaining perfect at *c*. The solution of sulphate of magne

sia is now to be connected with the negative pole of a battery by means of the platina plate *b*, and the water with the other pole of the battery by the plate *e*, which dips slightly inclined below the surface. When the circuit is completed, the sulphate of magnesia and the water are simultaneously decomposed, the oxygen appears upon the plate *b*, the hydrogen gas upon the plate *e*; but, although the sulphuric acid is liberated freely upon the plate *b*, no magnesia travels farther than the limiting surface of the saline liquor *c*. Here the metal *e* serves as a pole to the hydrogen, but not to the magnesia; and the water on which the magnesia has evolved has no power to prevent the farther passage of the hydrogen.

If A, C, B be filled with solution of sulphate of soda, and by means of the plates P and N, a current from a battery be passed through it, the acid will collect upon the one and the alkali upon the other plate: but if, by means of pieces of bladder, *a* and *b*, the vessel be divided into three compartments A, C, and B, and the central one being filled with a solution of sulphate of soda, dilute nitric acid is poured into those at the side in order to afford a conducting medium, the acid and alkali do not appear at the metallic poles when the current passes, but are evolved upon the inner surfaces of the partitions *a* and *b*: it is only when, by mechanical filtration, some of the liquor of C passes into A and B, that the slightest trace of sulphuric acid or of soda can be found upon the metallic plates.



By the electricity of the machine the same principle can be demonstrated: if a slip of paper moistened with solution of iodide of potassium be held near the insulated prime conductor of the electrical machine while in action, and the rubber be connected with the ground so as to ensure a continuous discharge of positive electricity into the air, iodine will be evolved in quantity upon the point of the paper nearest the prime conductor, while hydrogen and potash may be traced as far as any liquid conductor admitting of their passage goes. Here there is nothing that can be termed a pole; the iodine is discharged upon the limiting surface, which is here that of the atmospheric air.

Hence the idea of poles which produce attractions and repulsions in a closed circuit must be abandoned, and some other way of explaining the decomposition of the liquid elements of the circuit must be obtained. The word poles must first be laid aside, and the expressions proposed by Faraday in their place deserve universal adoption. The surfaces, whether of metal, of water, of acid, or of air, by which the current passes from one kind of conductor to another, he terms electrodes (*ηλεκτρον*, *οδος*), they being the routes through which the electricity makes its way. I shall therefore, in future, speak of the positive and negative electrodes in relation to the surfaces, generally of metal, by which the battery is brought to act upon the substance which is to be decomposed.

Since there are thus no attractive forces by which the chemical affinities of the substances in the decomposing cell can be overcome, to what mechanism can we attribute the separation of elements which occurs? Concerning this, as yet, there is only speculation to

be presented. The decomposition is certainly propagated from particle to particle, that is to say, at the moment that the molecule of water loses oxygen at the positive electrode, a different molecule gives off its hydrogen upon the negative electrode; neither the hydrogen of the former nor the oxygen of the latter become free, but the decomposition is transferred from one particle to another along the line, all particles of oxygen advancing a step against the current, and the molecules of hydrogen moving in a corresponding manner in the direction of it. Thus, if a line of particles of water in a decomposing cell be represented before the current passes, the electrodes being represented by the plus and minus signs, on the current passing, a molecule of oxygen will be evolved upon the positive, and one of hydrogen upon the negative side, as in the second line; and as this motion is participated in by every molecule of oxygen and hydrogen in the circuit, they will come into the final position of the third line. The current still passing, another molecule of each will be evolved, as in the fourth; and, ultimately, all the intervening water may be decomposed; the separation of the elements being thus accompanied by a continual rotation on each other of the intermediate molecules, each molecule of oxygen being successively united with every molecule of hydrogen in the series, and each molecule of hydrogen combining in turn with every particle of oxygen as it passes along. In Faraday's words, the current is an axis of power, equal, and exerted in opposite directions, by which, in every case of a true binary compound, the molecules of one element are carried in one direction, while those of the other constituent move in the reverse course.

$$+\mathrm{O.H.}\ \ \mathrm{O.H.}\ \ \mathrm{O.H.}-$$

$$-\mathrm{H.}\cdot\genfrac{}{}{0pt}{}{\mathrm{O.}}{\mathrm{H.}}\cdot\genfrac{}{}{0pt}{}{\mathrm{O.}}{\mathrm{H.}}\cdot\mathrm{O.}+$$

$$+\mathrm{O.H.}\ \ \mathrm{O.H.}-$$

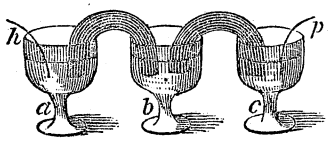
$$-\mathrm{H.}\cdot\genfrac{}{}{0pt}{}{\mathrm{O.}}{\mathrm{H.}}\cdot\mathrm{O.}+$$

$$+\mathrm{O.H.}-$$

From this idea, the evolution of the iodine, the soda, the magnesia on surfaces of air, of bladder, or of water, is easily understood. The sulphates of magnesia and soda are decomposed, because there exists in the solution a chain of particles of sulphuric acid capable of conveying their bases along, and these are evolved where that chain of acid particles is broken, although there may be other conductors to complete the circuit. The iodine is evolved where the air touches the surface of the paper, because the air has no potassium by which it could be carried farther. The decomposition appears thus to be effected, not by annulling chemical affinity, but with its assistance, for it is exactly with those conducting bodies whose elements have the strongest affinities for each other that decomposition is most easily effected. Thus iodide of potassium is decomposed much more easily than iodide of lead, yet the affinity of potassium for iodine is certainly greater than that of lead for the same element.

It is in this manner that arise the remarkable phenomena of transfer observed first by Humphrey Davy.

If a solution of sulphate of soda be placed in the glass *a*, dilute sulphuric acid in the glass *b*, and water in the glass *c*, and they be connected together with slips of amianthus, moistened to allow the passage of the current, and the positive electrode



of a battery be immersed in *a*, and the negative in *c*, the sulphate of soda will be decomposed, and its alkali will appear in *c*, although the acid in *b*, through which it must have passed, retains all its power. Here, then, was the affinity of the acid in *b* for soda completely annulled by the superior attraction of the negatively electric pole in *c*, and this was considered to be farther proved by the acid preventing the passage of barytes, for which its affinity was so much stronger; when *a* contained nitrate of barytes, the earth, on entering into *b*, combined with the sulphuric acid, and went no farther. But in these experiments, considered at the time so decidedly in favour of Davy's theory, that which was believed to be the obstacle to the passage of the soda is in reality the cause of it. Had there been no acid in *b*, no alkali could have passed across it, and the barytes remained combined only because, becoming insoluble, it no longer formed any portion of the liquid-conducting medium.

It has been, indeed, found, that although a feeble current may be transmitted through liquid conductors without any sign of de composition, yet, in general, the passage of a more powerful current can only be accomplished by means of bodies which are at the same time decomposed by its influence. Faraday proposes to term the decomposition by the current *electrolysis* [ηλεκτρον, λυω], and such bodies as undergo electrolysis *electrolytes.* It is, therefore, only electrolytes that are capable of conducting, and they do so by the opposite directions in which the chains of liberated particles move. That electrolysis may occur, it is necessary that the substance be in the liquid state, and hence all conducting power is lost when the body becomes solid; ice is a non-conductor, and it is only by being melted that the chlorides and iodides of lead and silver, and such bodies, become capable of conduction, and of being hence decomposed. But there are many bodies which insulate when cold, and yet, when heated, allow the current to pass even before they fuse, its passage being unattended by any electrolysis, even though the current be very powerful. Sulphuret of silver, iodide and chloride of mercury, and fluoride of lead, are remarkable examples of this anomaly.

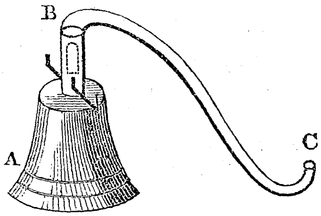
Faraday, considering that the words electro-positive and electro-negative involve too much those ideas of attractive and repulsive forces emanating from the poles, which have been proved to be incorrect, proposed some changes of nomenclature, which, if not adopted, deserve to be at least described. If we consider a voltaic battery lying on the ground, with the positive end to the east, and the wire connecting the ends bent into an arch, similar to that which the sun describes in his daily rotation, the current will flow up from the point of the sun's rising, and pass down into the battery opposite the point at which he sets. If the wire be now interrupted by a decomposing cell, the surface at which the current enters the liquid may be termed the *anode* (ἀνὰ, upward), and the other the *cathode* (κατὰ, downward); oxygen, chlorine, and such bodies are evolved upon the surface of the anode, while from the cathode hydrogen and the metals are liberated. The elements which, by their combination, form electrolytes, Faraday proposes to term *ions*, ἴημι, and to distinguish them into *anions* which pass to the *anode*, and *cations* which pass to the *cathode.* Electro-negative bodies are therefore *anions*, and electro-positive substances are *cations* in Far-

aday's nomenclature. These names are shorter, and involve less theory than the older terms, and hence deserve adoption.

The most important principle that has been as yet discovered, connecting the agencies of electricity and affinity, is the law of definite electro-chemical decomposition. If the same current of electricity pass through a series of electrolytes, it will decompose a quantity of each which is proportional to its chemical equivalent. Thus, at the same time and by the same force, there are obtained

8	grains of	Oxygen and	1	of Hydrogen	from	9	parts of	water.
35·4	“	Chlorine and	1	“ Hydrogen	“	36·4	“	muriatic acid.
35·4	“	Chlorine and	108	“ Silver	“	143·4	“	chloride of silver.
126·3	“	Iodine and	103·6	“ Lead	“	229·9	“	iodide of lead.

The principle of definite electro-chemical action may be applied to measure the quantity of electricity which is circulating in the current, for by collecting the substances evolved in the decomposing cell, we may obtain a standard to which all other effects may be reduced. In such case the decomposing cell becomes a *voltameter*, or measurer of voltaic electricity. One of its most convenient forms consists in a conical vessel, A, terminated by a tube, B, in the neck of which are soldered the platina electrodes in connexion with the battery; the vessel and tube being filled with water, which is rendered easily decomposible by the addition of sulphuric acid, the circuit is completed; a quantity of oxygen and hydrogen, proportional to the amount of electricity which passes, is evolved, and, issuing from the aperture at C, may be collected in an inverted glass and measured. A variety of other forms, not differing in principle, have been proposed and are in use.

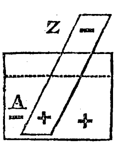


If the absolute identity of electrical and chemical agency be insisted on, then, in all electrolytes, the elements must be held together by the same force, since they require the same amount of electricity to produce decomposition; and we should return nearly to the principles of Berthollet, that chemical affinity was equally powerful for all bodies, and merely appeared to vary from external influences; but this would be a rash and unphilosophical conclusion; the electrolytes are but one class of chemical bodies, those which are primary compounds, of an equivalent of each element; the current does not act upon deutoxides or bichlorides, and on double salts its agency is exceedingly complicated. All that can be inferred from this very beautiful result is, that the elements of bodies combine, in separating from each other under the influence of a current, all with the same quantity of electricity, and that, as the specific heats of the ultimate particles of bodies have been already found to bear a simple relation to each other, the specific electricities may follow an equally, or still more simple law.

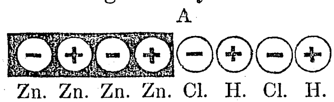
Having thus examined the important phenomena produced in the decomposing cell, the current being considered as originating in any sufficient source, we shall pass to the discussion of what occurs in the generating cell, where the current which passes through

the other is evolved by the mutual action of the liquid and solid elements of the voltaic battery.

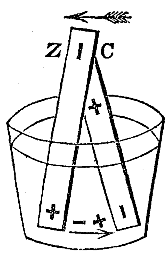
For the generation of the current, it has been already shown to be necessary that the liquid excitant should be an electrolyte, and that the solid elements should occupy positions in the electro-chemical scale as remote as possible from each other in relation to the liquid which is employed. That the solid elements also should be conductors, by which the selection is limited to the metals and to some forms of carbon. Now, when a slip of zinc is immersed in an electrolyte, which we shall, for simplicity, consider for the future



to be muriatic acid, the particles of the acid are brought into a state of excitation, the molecules of hydrogen becoming positively excited, and those of chlorine becoming negative. This condition has been already described (page 132) as being that of the acid particles; but it is now necessary to indicate more nearly the immediate manner in which it is produced. The mass of zinc itself, which we before considered as having, like a magnet, its positive excitation referrible to one, and its negative to the other extremity, must also, like the magnet, be looked upon as consisting of a great number of excited elements, each of which has its positive and negative extremities; or, for greater definiteness, they may be considered as grouped in pairs, of which one molecule is positively and the other negatively excited. The condition of the slip of zinc of the last figure may therefore be represented as in the figure at the

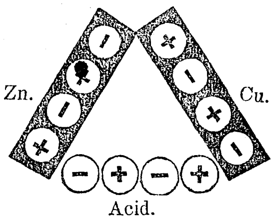


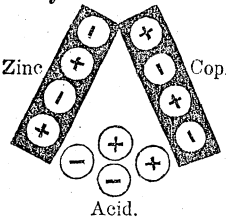
side, the particles of zinc being contained in the shaded bar, and those of the liquid, consisting of chlorine and hydrogen, represented outside of it. The terminal particle of zinc becoming positive, and the nearest particle of chlorine becoming negative, there would result immediate union if no other action interfered; but the chlorine is held back by the positive molecule of hydrogen with which it is united, and so the action continues balanced, no matter how far the series may extend on either side. If, now, the plate of copper be introduced so as to complete the circuit, and to allow the passage of the galvanic current, it is easy to see how the decomposition of the exciting fluid follows; for although, in the arrangement above described, the inductive excitement is most active at A, and diminishes from thence as it extends along the zinc upon the one hand, and



through the fluid upon the other, yet when, as in the figure, the circuit is completed, the action becomes equally powerful all through; the particles of copper assume a condition similar to those of the zinc, but in the reverse order, the molecule next the acid being negative, and that becoming positive which is in contact with the zinc, and hence a complete chain of inductively polarized particles being established, precisely such as are represented by cuttings of silk thread which convey a current from an electric machine through oil of turpentine; the molecular arrangement being represented in the following figure. Such be-

ing the position of the mutually-excited molecules, the electricities of the particles of zinc and chlorine nearest to each other combine, and their neutralization is followed by that of the entire chain; the adjacent particles of zinc and chlorine then unite, and the hydrogen, disengaged, is thrown upon the second particle of chlorine, its hydrogen upon the third chlorine molecule, by which the hydrogen it had previously been united with, being thrown off, is emitted under the form of gas.





The three distinct stages in this reaction are, therefore, 1st, The mutual excitation, by inductive polarization of the zinc and muriatic acid. This is the fundamental fact due to the chemical relations of these bodies. 2d, The completion of the chain of inductively polarized particles, by the intervention of the copper plate and connecting wire. 3d, The passage of the current, and the consequent decomposition of the liquid electrolyte in the cell, the chlorine being evolved upon the zinc, with which it enters into combination, and the hydrogen being eliminated upon the surface of the copper plate.

The source of the current is therefore not to be found in the decomposition of the acid, for it precedes it; but the quantity of chemical action in the generating cell is proportional to the quantity of electricity which passes, for it is produced entirely by its agency. There is, therefore, no difference in reality between the generating and the decomposing cell; the action in each is equally produced by the passage of the electric current; but in the generating cell, one element at least, the chlorine, is absorbed by the electrode (the zinc) on which it is evolved, and the amount of obstacle presented to the passage of the current is proportionally less.

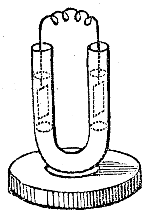
Such is the theory of galvanism which I believe to be most consistent with all the results hitherto obtained. The current cannot have its origin in the contact of solid bodies, for it remains the same, no matter how much the circumstances of contact may be changed; and by every alteration of the conditions of chemical action, it varies in direction and in power, although the relations of the solid bodies which are in contact are not affected. Neither does the current arise from the transfer of elements which occurs in the generating cell, for, on the contrary, the transfer of elements results from the passage of the current, indicating its direction and measuring its amount; but the current arises from the continuous restoration through the copper, or positive element, of the excitation produced by the tendency of the zinc to combine with the chlorine of the muriatic acid. In fact, although I have hitherto considered the zinc as only influencing the acid by means of a disposition to unite with one of its constituents, yet such expressions, being rather abstract and indefinite, may in the present case be laid aside. The zinc does, on immersion, decompose a certain quantity of acid, of which the hydrogen is evolved in the form of gas, constituting upon the sur-

face of the zinc an exceedingly thin layer. The chlorine is then in a state of combination, which is not without analogy in other cases; that is, in presence of two substances for which its affinity is equally intense, it is disposed to unite with either, according as external forces intervene, and is determined to the zinc by the establishment of the current.

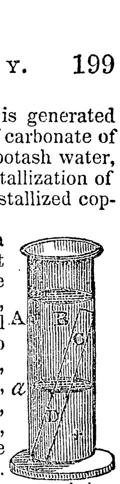
The proofs that hydrogen must be thus *nascently* liberated upon the surface of the zinc are to be found in a phenomenon already noticed under the head of affinity—the precipitation of one metal from its salts by means of another having a greater affinity for oxygen than it. If we immerse in a solution of sulphate of copper a slip of pure zinc, there is instantly a deposition of copper, which we must ascribe to the superior affinity of zinc for oxygen and sulphuric acid; but when the zinc has become thus sheathed in metallic copper, the decomposition would cease, by the access of the acid being prevented, were it not that the copper deposited acts as the copper element of a galvanic circuit, and the subsequent decomposition proceeds, each new portion of copper being deposited on the outside, farthest from the zinc, the action of which becomes thus at every moment more intense. If hydrogen had a physical constitution, such as would enable it to act as the positive element of a simple galvanic circle, then, no doubt, the purest zinc would decompose the muriatic acid, the circuit being completed by the hydrogen evolved; but such is not the case, owing to its gaseous form; but it being that alone which is the obstacle, the previous step, which depends simply on the chemical affinity of hydrogen and chlorine, may reasonably be considered to have occurred.

The action of electricity in separating the elements of bodies is scarcely of greater interest or importance from the ideas it suggests of the nature of chemical affinity, than it becomes as a means of presenting to each other, under the most favourable circumstances for union, the different elements of the voltaic circuit, and thus causing the formation of bodies for whose construction the ordinary processes of the laboratory are much too violent and abrupt. In this way some of the most remarkable substances of the mineral kingdom may be artificially produced, the secretion of the metalliferous ores into the veins and cavities of rocks accurately represented, and bodies, whose affinities for each other rank as the most intense, completely, though silently and gradually, separated from each other. It is to Becquerel that we owe almost all our knowledge of this important function of electricity; from him we have also received the important lesson, that it is not in the brilliant effects of the great batteries of Davy or of Daniell that we must seek a clew to the history of the electrical processes of chemical affinity, but in the slow but unintermitting action of currents of such low intensity that a drop of pure water would be an insuperable obstacle in their path. The electricity to be employed in the artificial formation of compound bodies must be such as is generated by a single pair, and these generally of metals whose similarity prevents that current from being of great amount.

These phenomena, into the examination of which I cannot enter with much detail, are best observed by means of a tube bent into a U shape, and at the bottom of which is interposed a porous partition of clay or plaster of Paris; the liquids, whose mutual reaction is to generate the new substance, are placed in the legs of the tube, one at each side of the partition, through the pores of which they gradually mix with each other. The voltaic current is then supplied either by connecting the liquids with the poles of a feeble battery, or by immersing in one leg a zinc, and in the other a copper or platina plate, connected by a wire with each other. If a solution of carbonate of soda and of sulphate of copper be thus brought to act on one another, a double carbonate of copper and soda crystallizes on the plate immersed in the copper liquor; and if then

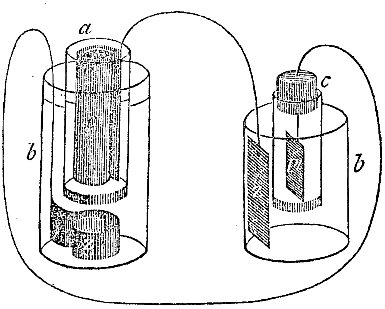


the solution of soda be replaced by ordinary water, a new current is generated which decomposes the first product, and forms a new crystallization of carbonate of copper. If the zinc leg be filled with a solution of oxide of zinc in potash water, and a solution of nitrate of copper be placed on the copper side, a crystallization of oxide of zinc is produced upon the zinc plate, and a deposition of crystallized copper upon the metallic surface in the other tube.



By using two liquids which have unequal chemical actions on a strip of metal, this may be made to precipitate itself, being reduced at one extremity according as it is dissolved at the other. Thus, if the glass A be filled with solution of nitrate of copper to *a*, and then water, rendered slightly acid by nitric acid, be gently added, up to the level of B, a slip of copper, introduced so as to present equal surfaces to the two liquids, generates a current which passes up through its mass, and down from the lighter to the denser fluid: the copper dissolves, therefore, above, and the salt formed being electrolyzed by the current, its metal is deposited on the lowest surface under the form of crystals, and this is continued until the free acid, and hence the electromotive force in the liquid, becomes equal, when, of course, no current passes.

Dr. Bird, who has extended considerably the results obtained by Becquerel, has constructed an apparatus for such reactions, with which he has obtained, in an isolated form, those simple bodies, as boron, silicon, potassium, &c., whose compounds resist ordinary means most obstinately. It consists of a generating and of a decomposing cell. This last is a glass cylinder, *a*, within another glass cylinder, *b*. The inner one, *a*, is four inches long, and an inch and a half in diameter, and is closed at the lower end by a plug of plaster of Paris, 0·7 inch in thickness. This cylinder is supported within the other, *b*, which is an ordinary jar, about eight inches deep and two inches diameter, by means of wedges of cork. A piece of sheet copper, *c*, four inches long and three inches wide, having a copper conducting wire soldered to it, is loosely coiled up and placed in the inner cylinder, while



a piece of sheet zinc, of equal size, is also coiled up and laid on the bottom of the outer cylinder, it being also furnished with a conducting wire. The outer cylinder is then to be nearly filled with a weak brine, and the smaller with a saturated solution of sulphate of copper; the two fluids being prevented from mixing by the plaster of Paris diaphragm. After it has been in action for some weeks, chloride of zinc is found in the external cylinder, and beautiful crystals of metallic copper, frequently mixed with the ruby protoxide (closely resembling the native ruby copper ore), and large crystals of sulphate of soda, are found adhering to the copper plate in the smaller cylinder, especially on that part where it touches the plaster diaphragm. The apparatus is completed by the decomposing cell, which is, in fact, a counterpart of the battery itself, consisting, like it, of two glass cylinders, one within the other, the smaller one having a bottom or floor of plaster of Paris fixed into it; this smaller tube may be about half an inch wide and three inches in length, and is intended to hold the metallic solution submitted to experiment, the external tube, *b*, into which it is immersed being filled with a weak solution of common salt. Into the latter solution, a slip of amalgamated zinc (for the positive electrode), soldered to the wire coming from the copper plate of the battery, is immersed, while for the negative electrode, a slip of platina foil, fixed to the wire from the zinc plate of the battery, passes through a cork, *c*, fixed in the mouth of the smaller tube, and dips into the metallic solution it contains.

The influence which electricity thus exercises upon affinity, and the modifications in its results producible by its means, although proving a most intimate connexion, do not go, as I believe, so far as to demonstrate a complete identity of cause. It is possible that, hereafter, some sublime generalization may embrace the phenomena of heat, of light, and of electricity, of cohesion and gravity, as well as of chemical affinity, within one law, and indicate how, by varied manifestations of a single agent, their separate peculiarities may arise; but, though we may look forward to

such a state of science, we dare not rashly seek to anticipate its approach; and I look upon electricity as producing and being produced by chemical phenomena, precisely as we find heat to influence as well as to be evolved by chemical combination.

Where electricity is brought into play so powerfully by the action of a simple body upon a compound fluid, it is, I consider, unreasonable to imagine that, in the combination of simple bodies, or of compound bodies with each other, no electricity should be set free, particularly when it is proved that in such cases some electricity does appear, although in quantity bearing no proportion to that of the feeblest galvanic battery. If I were to suggest an electro-chemical theory, such as might agree with the facts that have hitherto been discovered, I should consider that bodies in their free state are perfectly destitute of excitation; but that chemical union, or the degree of intimate approximation which precedes union, may be a source of electrical disturbance, and is that which, in all ordinary cases, gives origin to the electricity employed in our experiments. When united, bodies are likewise destitute of electrical properties; in iodide of potassium, the bond is the affinity of iodine and potassium for each other, and not that the iodine is in a permanent state of negative excitation while the potassium remains positive.

If hydrogen gas be burned in oxygen, there is evolution of electricity, of which only a trace escapes immediate recombination under the form of light and heat, but the existence of which, in a highly intense form, has been demonstrated by Pouillet. The oxygen and the vapour of water produced assume the positive condition; the residual hydrogen becomes negative. If carbon be burned in oxygen, there is likewise combustion and evolution of electricity, of which the positive passes off with the carbonic acid, and the negative rests upon the carbon. The evolution of heat may be in these cases an independent effect of combination, but I would look upon it as being more probably the result of the union of the electricities evolved. If the bodies which act upon each other are dissolved in water, there is no combustion, but heat is still evolved, and the electricities unite with one another without the necessity for any intermediate circuit. It is only where the replacement of one body by another occurs, that the establishment of the chain of inductively polarized molecules becomes necessary; for the particles of zinc and hydrogen, which become oppositely united, have no power to combine, and hence cannot be restored to neutrality unless by the medium of a third body, to which both may impart their excitations. That the zinc and hydrogen upon the one hand, and the copper and hydrogen upon the other, do not unite, is, I conceive, fatal to those views which assume the identity of chemical and electrical, or, as they call it, current or inductive affinity; for if a molecule of copper in the acid stood in the place of, and acted as a molecule of chlorine, it should unite with the hydrogen in place of allowing it to pass off free.

The act of chemical union being such as to produce electrical excitation and discharge before it is completed, and the permanent combination of the elements being the result of the return to the neutral state, it is easy to understand that, when these conditions are reversed, the chemical affinity should be superseded, and the bodies brought into the state in which they had been at the moment of excitation, and while their elements, oppositely excited, were yet separate from each other. A compound body is therefore, as I apprehend, decomposed by the battery, from having this electrical state given to it by the current; and the transfer of its elements across the liquid is accomplished by a series of neutralizations and excitations, accompanying the unions and decompositions by which they pass to the electrodes, on which they yield up their ultimate excitation, and appear isolated and completely neutral. The quantity of electricity necessary to decompose a body is therefore the same as it had evolved when its elements entered into union, and it should hence follow that the current of electricity evolved in the union of chemical equivalents of the simple bodies with each other should be the same. That this actually occurs appears probable from the analogy of heat; an equivalent of oxygen, in combining with various metals, evolves the same quantity of heat, and if the heat be a consequence of the neutralization of electricity, the quantity of this evolved should be the same also. It appears, likewise, that an equivalent of sulphuric acid, in combining with different bases, evolves the same quantity of heat, and to decompose the various salts thus formed, the same quantity of electricity should be required; and hence, that the two actions, so completely equivalent to each other, may satisfactorily be referred to the same source.

Such is the interpretation I put upon the phenomena of electro-chemical decom

position, and the relations of electrical forces to affinity. In the molecular condition of polar excitation which accompanies the passage of a current, I adopt fully the peculiarly explicit mode of representing he actions of the bodies on each other proposed by Graham, but I consider it too hypothetical to assume that such molecular state naturally exists in bodies; it may or it may not; but in the absence of evidence that it does, I am not inclined to presuppose it unnecessarily. I look upon the current as being produced by the union of opposite polarities, which are themselves not the cause, but the consequence, of the chemical affinities of bodies. Graham is not disposed to admit that the union of simple bodies may be accompanied by an electrical phenomena, and to exclude also from the application of an electro-chemical theory the combination of acids and of bases with each other, as not capable of generating currents; but the reason of this is, as I imagine, that the currents so generated are necessarily closed.

In concluding the admirable treatise on electricity with which he has enriched scientific literature, M. Becquerel details the views which he has adopted regarding the electro-chemical relations of bodies; and although they are not expressed with the definiteness which might be wished from so admirable a philosopher, I shall endeavour, in concluding this section, to give a short description of them. In the main, they do not differ much from the principles of electro-chemical combination which I have long since adopted, and which have been already noticed.

M. Becquerel considers that in all bodies there is distributed a quantity of electricity indefinitely great, which is so intimately connected with their molecular constitution, that it is disturbed, and excitation produced in all cases where molecular disarrangement is produced; hence pressure, friction, an unequal distribution of heat, &c., are sources of electricity.

Chemical affinity is also a source of electrical disturbance. When an acid combines with an alkali, the first sets free positive electricity, and the second an equal quantity of negative electricity; these two combine immediately in the liquor, forming neutral fluid, and produce as many currents as there had been particles in action; now this multitude of little currents ought to determine the production of a quantity of heat, depending on the energy with which the affinity was manifested, and the conducting power of the liquid. In decompositions, the electrical effects are inverse, that is, the acid takes the negative, and the alkali the positive electricity; hence it may be concluded, as M. Becquerel had already stated with regard to aggregation, that if electricity does not constitute affinity, it is at least indispensable to its manifestation, since it is always subjected to the same laws every time that simple or compound atoms unite or separate. From all considerations, it appears that the electricity produced by chemical action is only an effect resulting from the action of the affinities brought into play; and this effect being brought into inverse action in decomposition, announces at the same time a molecular electric state, indispensable to the permanent union of the elements of compound bodies.

To explain decomposition by a current of electricity, M. Becquerel adopts Ampere's idea of electrical atmospheres, although he denies that any bodies are naturally or permanently in a positive or negative condition; but he supposes that the neutral condition of a body consists in the molecule being either positive or negative, and being surrounded by an atmosphere in an opposite state. When bodies unite, the union of their atmospheres produces light and heat, and the molecules remain excited while in union, although the union is the cause of the electrical disturbance, and not its effect. Now, when zinc is put in contact with water, this last is decomposed, and there is hence a disturbance of electricity; the particle of zinc abandons its negative atmosphere, and unites in a positive condition with the negative and nascent oxygen; the hydrogen is liberated nascent also, and highly positive; in this state the oxygen would be balanced between the two equally positive particles of zinc and hydrogen, and the decomposition could not proceed; but, if a slip of copper be introduced, this supplies a negative atmosphere to the hydrogen, which, becoming neutral, is evolved as gas, and, transferring its positive electricity to the point of contact with the zinc, neutralizes its excess of negative excitement, and generates the current. M. Becquerel refers the chemical action of the current in the decomposing cell to each electricity setting the same electricity of the compound in motion in the same direction with which the particles are transferred by a series of combinations and decompositions, as has been already described, until the limits of the substance are attained, and then the elements are evolved in the neutral state.

M. Becquerel has endeavoured to apply the agency of electricity to determine the

relative affinities which bodies have for each other. His principle is as follows: if nitrate of copper and nitrate of silver be dissolved together in equal quantities, and decomposed by a galvanic current, the nitrate of silver alone is at first affected, because the affinity of the silver for the oxygen and acid is so much less than that of the copper for the same. But, when the quantity of nitrate of copper is gradually increased, a term is arrived at when the electric current is exactly equally divided between the two metals, the greater quantity of copper making up for the greater resistance it offers to the decomposing power. His results are, that when the solution contains twenty parts of copper to one of silver, the current acts equally on both; when the copper is 25 to 1, the current acts as if it divided itself $\frac{2}{3}$ to the copper and $\frac{1}{3}$ to the silver; and when the quantity of copper is thirty times that of the silver, there are three equivalents of the copper salt decomposed for one of the salt of silver. M. E. Becquerel has essayed the same important problem in a different way, by testing the power of solutions of chlorine, iodine, and bromine, to absorb nascent hydrogen and nascent oxygen, evolved in their mass by means of a galvanic current. His results appear to show that the affinities are expressed by the numbers; for

Hydrogen.		*Oxygen.*	
For Chlorine	922	For Chlorine	169
Bromine	712	Bromine	380
Iodine	212	Iodine	469

These two series are, however, independent of each other, and afford no mutual term of comparison whatsoever.

It is to be trusted that such investigations, conducted with the ingenuity and accuracy which the Becquerels can so well apply, may lead to results of the highest interest to science. The reduction to numerical laws of the influence of quantity on affinity, and the determination in numbers of the tendencies of the simple bodies to unite, would certainly advance the condition of chemistry, as an exact science, in a remarkable degree.

CHAPTER IX.

ON THE LAWS OF COMBINATION.

THE general nature of affinity, and the modifications which it undergoes from the influence of the physical agents, having been now stated, I shall proceed to discuss the numerical laws to which its results are subjected, the discovery of which was the first step in conferring upon chemistry the character of an exact science.

It is characteristic of chemical affinity, that the proportions in which bodies are brought to unite by its agency are limited upon both sides, whereas, in those cases where molecular forces alone prevail, the proportions, although perhaps limited in one direction, are indefinite in the other. Thus a saturated solution of chloride of sodium cannot take up any more salt, but it may be mixed with any quantity of water, whereas the chloride and the sodium, which constitute the salt, form it only in certain proportions which are invariable, 100 parts containing always 39·66 of sodium and 60·34 of chlorine. If it were not for this constancy of proportion, the science of chemistry could never have advanced beyond its merest elements; for, had chlorine and sodium been capable of combining in all indeterminate proportions, or had the properties which we recognise in chloride of sodium been ascribable to compounds of those elements

in every possible proportion, no accurate ideas regarding the constitution or properties of bodies could have been acquired, and none of the benefits derivable from experience or experiment could have been attained. The first law of constitution is, therefore, that the composition and properties of any given substance are always the same.

When, by the intervention of superior affinities or by double decomposition, a compound body is decomposed and a new compound formed, the proportions by weight of the various substances brought into action have a constant relation to one another, and, as they represent the quantities of the bodies which exercise equal, or, at least, equivalent combining powers, they are termed, when reduced to numbers, the combining proportions or equivalents of these bodies. Thus, if 100 parts of oxide of copper be heated in a current of hydrogen gas, it is reduced, and the hydrogen, uniting with the oxygen which it contained, forms water. In the 100 of oxide there were 79·83 of metallic copper and 20·17 of oxygen, which last, taking 2·52 of hydrogen, forms 22·69 of water. Now, in this case, the 2·52 of hydrogen produce the same result of satisfying the combining power of the 20·17 of oxygen as the 79·83 of copper; and hence these quantities of hydrogen and copper are equivalent to each other. This example may be, however, brought much farther. If, in place of treating the oxide of copper by hydrogen gas, it had been acted on by chloride of hydrogen, the oxygen should have been carried off by the hydrogen, which would abandon its chlorine for that purpose; but the chlorine should not be set free; it, on the contrary, would unite with the copper from which the oxygen had been taken, and the reaction would be so proportioned that the quantity of copper reduced by the hydrogen of the chloride of hydrogen would be exactly sufficient to unite with all the chlorine which was therein contained, and form with it chloride of copper. In this case the 100 parts of oxide of copper would require for its decomposition 91·73 of chloride of hydrogen, and there would be formed 169·04 of chloride of copper and 22·69 of water. Here, as before, the 20·17 of oxygen uniting with 79·83 of copper and 2·52 of hydrogen, show their equivalency; but we learn in addition, that 79·83 of copper and 2·52 of hydrogen unite equally with 89·21 of chlorine, and hence that that quantity of chlorine corresponds, and is equivalent in combination, to 20·17 of oxygen.

Starting from this point, we may proceed to a still more extended range of instances. If we treat sulphuretted hydrogen gas with iodine, we find that it is totally decomposed, sulphur being precipitated, and iodide of hydrogen being formed. Now, taking the quantity of the sulphuret of hydrogen, containing the weight obtained in the former example, 2·52 of hydrogen, we find it to be 43·09, and hence to contain 40·57 of sulphur, which separates by the action of the iodine, of which 318·28 parts, uniting with the 2·52 of hydrogen, form 320·79 of iodide of hydrogen. If this iodide of hydrogen be next treated with chlorine, it abandons its iodine, and forms 91·73 of chloride of hydrogen.

Setting out, therefore, from 100 parts of oxide of copper, and tracing its elements through a variety of decompositions, in all of

which the quantities engaged effect the same purpose of satisfying the tendency to combine, we found for the numbers which express the equivalent quantities of the simple bodies employed the following:

Copper	79·83	Chlorine	89·21
Hydrogen	2·52	Sulphur	40·57
Oxygen	20·17	Iodine	318·28

and as the compound bodies formed are also equivalent, from their being produced by the same, or equivalent combining actions, we may express also in numbers their combining proportions thus:

Oxide of copper	100·00	Sulphuret of hydrogen	43·09
Oxide of hydrogen	22·69	Iodide of hydrogen	320·79
Chloride of hydrogen	91·73	Chloride of copper	169·04

It is evident that if, in place of oxide of copper, any other metallic oxide reducible by hydrogen had been employed, its equivalent should have been obtained, and in this way the equivalents of the majority of metals have been determined.

These numbers are quite arbitrary; and any other body in the list might as well have been taken for the origin as oxide of copper. In practice such numbers are reduced to a standard, which is taken as 1 or 100, and for this purpose, oxygen or hydrogen, the most important bodies, are selected.

Any number experimentally obtained, as the above, may be reduced to the standard scale by the rule of simple proportions: thus, the equivalent of copper being 79·83, oxygen being 20·17, and hydrogen 2·52, it is

$$20{\cdot}17 : 79{\cdot}83 :: 100 = 395{\cdot}7 \quad \text{Oxygen} = 100$$
$$\text{and } 2{\cdot}52 : 79{\cdot}83 :: 1 = 31{\cdot}71 \quad \text{Hydrogen} = 1$$

It is difficult to decide which of the two scales thus formed deserves preference: the hydrogen scale has been, by the authority of Davy, so long prevalent in these countries, that it is difficult to supersede it; and it possesses the advantage that hydrogen has the smallest equivalent of all bodies. The standard of oxygen is, however, for use, the more convenient, as, in consequence of the great preponderance of bodies in which oxygen exists, the calculations are much simplified by its number being 100; and there are but two or three bodies which, on that scale, require to be expressed in a fractional form.

When the study of these equivalent proportions first occupied the minds of chemists, Doctors Prout and Thompson were led, from speculations regarding the physical constitution of gaseous bodies, to suggest that the equivalent numbers of all substances were simple multiples of that of hydrogen; and as, representing hydrogen by 1, the other numbers therefore became all whole numbers, the scale acquired thereby considerable simplicity. The researches of Berzelius appeared, however, to controvert that hypothesis; and in his numbers, which are, for the most part, those given in the following list, no trace of such a law can be detected: later researches have also, in the hands of Turner and of Penny, afforded additional support to this opinion; but Phillips has lately reopened the discussion, and Dumas is inclined to consider the original views of Prout as being probably correct. In any case, the numbers given

in the list must be looked upon as being, in a slight degree, still open to revision.

In the following table, the equivalents of all the simple bodies are expressed on each of these scales; and throughout this work the two equivalent numbers will be given for each compound body, except where it is otherwise remarked.

Names of Elements.	Equivalents. O.=100	H.=1	Names of Substances.	Equivalents. O.=100	H.=1
Aluminum . . .	171·2	13·7	Mercury	1265·8	101·43
Antimony . . .	1612·9	129·2	Molybdenum . .	598·5	47·96
Arsenic	940·1	75·34	Nickel	369·7	29·62
Barium	856·9	68·66	Nitrogen . . .	175·0	14·00
Bismuth . . .	886·9	71·10	Osmium . . .	1244·5	99·72
Boron	136·2	10·91	Oxygen	100·0	8·01
Bromine . . .	978·3	78·39	Palladium . . .	665·9	53·36
Cadmium . . .	696·8	55·83	Phosphorus . .	392·3	31·44
Calcium	256·0	20·52	Platinum . . .	1233·5	98·84
Carbon	76·0	6·08	Potassium . . .	489·9	39·26
Cerium	574·7	46·05	Rhodium . . .	651·4	52·2
Chlorine . . .	442·6	35·47	Selenium . . .	494·6	39·63
Chromium . . .	351·8	28·19	Silicon	277·3	22·22
Cobalt	369·0	29·57	Silver	1351·6	108·3
Columbium . . .	2307·4	184·90	Sodium	290·9	23·31
Copper . . .	395·7	31·71	Strontium . . .	547·3	43·85
Fluorine	233·8	18·74	Sulphur	201·17	16·12
Glucinum . . .	331·3	26·54	Tellurium . . .	801·76	64·25
Gold	2486·0	199·21	Thorium . . .	744·9	59·83
Hydrogen . . .	12·5	1·00	Tin	735·29	58·92
Iodine	1579·5	126·6	Titanium . . .	303·66	24·33
Iridium	1233·5	98·84	Tungsten . . .	1183·0	94·80
Iron	339·2	27·18	Vanadium . . .	856·9	68·66
Lanthanum . .			Uranium . . .	2711·4	217·26
Lead	1294·5	103·73	Yttrium	402·5	32·25
Lithium	80·3	6·44	Zinc	403·2	32·31
Magnesium . .	158·3	12·69	Zirconium . . .	420·2	33·67
Manganese . . .	345·9	27·72			

The determination of the equivalents of compound bodies is an equally remarkable application of the principles that have been laid down. The equivalent number of a compound is the sum of the equivalent numbers of its constituents, as has been already seen in the numbers obtained for the oxides and chlorides of copper and of hydrogen. In this way may be constructed lists of the equivalents of compound bodies; thus, reducing the substances already noticed to the scales, there are:

Substances.	Equivalents. O.=100	H.=1	Substances.	Equivalents. O.=100	H.=1
Oxide of copper . .	495·7	39·72	Chloride of copper .	838·3	67·18
Oxide of hydrogen .	112·5	9·01	Iodide of hydrogen .	1592·0	127·57
Chloride of hydrogen .	445·1	36·47	Sulphuret of hydrogen	213·7	17·12

It is in relation, however, to the mutual decomposition of saline bodies that the principle of equivalent proportion becomes of most interest, and by which it is best illustrated. If to a solution of nitrate of barytes we add a solution of sulphate of soda, there is immediate decomposition, by the mutual interchange of acids and bases, and the neutrality of the solution remains completely undisturbed; the salts which exist after mixture are equally neutral with

those which had existed previously, and the quantities of acids and bases which are involved in the decomposition are hence equivalent to each other. Thus, if we take 130·7 parts of nitrate of barytes, we find that they require for their decomposition exactly 71·3 parts of dry sulphate of soda, and that there are formed 116·7 parts of sulphate of barytes and 85·3 parts of nitrate of soda. The composition of these four salts is:

Sulphate of Barytes.		*Nitrate of Soda.*	
Sulphuric acid . .	40	Nitric acid . . .	54
Barytes	76·7	Soda	31·3
	116·7		85·3
Nitrate of Barytes.		*Sulphate of Soda.*	
Nitric acid . . .	54	Sulphuric acid . .	40
Barytes	76·7	Soda	31·3
	130·7		71·3

All four are neutral; the acids and bases are in all equally neutralized, and hence the 40 of sulphuric acid and 54 of nitric acid, being capable of saturating the same quantity of base, whether it be soda or barytes, are equivalent quantities, and represent the combining proportions of these acids; and the 76·7 of barytes and the 31·3 of soda being likewise shown to possess equal powers of neutralizing the acid, whether nitric or sulphuric, are the numerical equivalents of those bases. If there had been a larger quantity of either salt present, it would have remained unaffected, the interchange of elements taking place only in equivalent proportions. Had nitrate of lead been employed in place of nitrate of barytes, the proportion necessary would have been different, and a different quantity of sulphate of lead would have been produced from the same sulphate of soda. Thus, to the 71·3 of sulphate of soda, there should be,

Nitric acid . .	54·0,	producing	Sulphuric acid . .	40·1
Oxide of lead .	111·7,	"	Oxide of lead . . .	111·7
Nitrate of lead	165·7		Sulphate of lead	151.8

If, in place of sulphate of soda, we take oxalate of soda, we shall find that 67·3 of it will exactly fulfil the functions of 71·3 of sulphate of soda, and these, consisting of 31·3 of soda and 36·0 of oxalic acid, will, by decomposing 130·7 of nitrate of barytes or 165·7 of nitrate of lead, produce 147·7 of oxalate of lead or 112·7 of oxalate of barytes. 36 of oxalic acid are therefore equivalent to 40·1 of sulphuric acid and 54·0 of nitric acid.

A table of equivalents of acids and bases might thus be drawn up: there should be,

Substances.	Equivalents. O. = 100.	Equivalents. H. = 1.	Substances.	Equivalents. O = 100.	Equivalents. H. = 1
Nitric acid . .	677·0	54·0	Soda	390·1	31·3
Sulphuric acid .	501·1	40·1	Barytes . . .	956·9	76·7
Oxalic acid .	452·9	36·0	Oxide of lead .	1394·5	111·7

It was in this form that the equivalency of different quantities of chemical substances was first recognised, and numbers assigned with extraordinary skill, by Wenzel, whose labours, although overlooked at the time, must be considered as the first and greatest step towards assigning the numerical conditions of chemical action.

The mode of determining the equivalent number of a new substance can now be easily understood. If it be an acid, it is to be combined with some base of which the equivalent is known; if it be a base, it must be united with an acid. If it be a metal, it may be united with chlorine or oxygen. If it be a simple non-metallic body, it may be united with a metal. In any case, a well-defined compound of the new body with one whose equivalent number is already known must be obtained and accurately analyzed. The equivalent numbers of the two bodies are proportional to the quantities in which they were combined, provided we have reason to consider that the compound examined contained an equivalent of each. Thus, if the new body form with sulphuric acid a perfectly neutral and soluble salt, and, on analysis, this yields 37·3 of sulphuric acid and 62·7 of the new base in 100, the equivalent is found by the proportion, as, 37·3 : 62·7 : : 40·1 : x=67·4, which is the equivalent of the body, 40·1 being that of sulphuric acid, and hydrogen being =1.

A calculation of this kind requires, however, to be checked by a knowledge of the next law of combination, that of multiple proportions; for, as has been stated, we presume, in the example, the salt analyzed to be composed of an equivalent of each constituent. It may be, however, that it contained two equivalents of acid to one of base, in which case the number for the latter would become 134·8; or two equivalents of base to one of acid, which would make the number 33·7. The proportions might be even still more complex; and hence, before attempting to decide on the equivalent number of a body, its general history must be studied.

The third law of combination is, that where one body unites with another in more proportions than one, there exists a simple relation between the quantities of the second, which, in the different compounds, unite with the same quantity of the first. Thus, taking manganese and nitrogen, which are remarkable for the number of compounds which they form with oxygen, there are,

345·9	of manganese unite with	100	of oxygen, forming	protoxide.
345·9	"	150	"	sesquioxide.
345·9	"	200	"	peroxide.
345·9	"	250	"	manganous acid.
345·9	"	300	"	manganic acid.
345·9	"	350	"	permanganic acid.

And with nitrogen,

175	of nitrogen unite with	100	of oxygen, forming	nitrous oxide.
175	"	200	"	nitric oxide.
175	"	300	"	hyponitrous acid.
175	"	400	"	nitrous acid.
175	"	500	"	nitric acid.

Here the successive quantities of oxygen taken by the manganese are as the numbers 2, 3, 4, 5, 6, 7, and those which combine with the nitrogen are as 1, 2, 3, 4, 5. In the last case they are all simple multiples of the first proportion, but in the case of manganese they are multiples of one half of the quantity contained in the protoxide. The analogy of some other similar bodies, however, renders it extremely probable that, though it has not been yet discovered, there

exists a compound of 348·9 of manganese with 50 of oxygen, and this should then be the first term of the series.

This law of multiple proportions holds not only with regard to the simple bodies already stated, but also with compound bodies of every class. Thus chromic acid combines with potash in three different proportions, forming by

52·2 chromic acid	+47.3	potash,	neutral chromate of potash.
104·4 "	+47·3	"	bichromate of potash.
156·6 "	+47·3	"	terchromate of potash.

Sulphuric acid combines with potash in two proportions,

40·1 sulphuric acid	+47·3	potash,	neutral sulphate.
80·2 "	+47·3	"	bisulphate.

It was, indeed, by the verification of it in the carbonates and oxalates of potash by Wollaston, that this law obtained in the first instance general acceptation.

22 of carbonic acid	+47·3	potash, form	carbonate of potash.
44 "	+47·3	"	bicarbonate of potash.
36 of oxalic acid	+47·3	potash, form	oxalate of potash.
72 "	+47·3	"	binoxalate of potash.
144 "	+47·3	"	quadroxalate of potash.

In salts with excess of base, the same principle holds. Thus, in the sulphates of copper, I have shown that

39·7 oxide of copper	+40·1	sulphuric acid, form	neutral sulphate.
79·4 "	+40·1	"	bibasic sulphate.
158·8 "	+40·1	"	quadribasic sulphate.
317·6 "	+40·1	"	octobasic sulphate.

In other cases the series, though not so complete, evidently follows the same law.

The great use of the symbolical nomenclature, noticed already in page 156, consists in its supplying an exact expression of this law of multiple proportions. The ordinary symbol of a simple body indicating an equivalent of it, the number by which that symbol is multiplied, in the formula of each compound body, represents the number of equivalents therein contained. Thus, for manganese and nitrogen, already used as instances, the symbolical expression of the law is given in

N.O. Nitrous oxide.	Mn.O. Protoxide of manganese.
$N.O_2$ Nitric oxide.	Mn_2O_3 Sesquioxide.
$N.O_3$ Hyponitrous acid.	$Mn.O_2$ Peroxide.
$N.O_4$ Nitrous acid.	$Mn.O_3$ Manganic acid.
$N.O_5$ Nitric acid.	Mn_2O_7 Permanganic acid.

The numerical coefficient is sometimes placed, as here, below and to the right of the letter symbol; by other chemists it is placed to the left and on the same line, as Pb.+2O. Cr.+3O., and sometimes to the right and above the letter, as $Pb.O^2$ $Cr.O^3$. This makes no difference in chemistry; but the student must be careful not to confound chemical with mathematical symbols, in which the position of the number might alter its power and meaning altogether. It must be noticed, however, that numbers written as the above affect only the immediate symbol to which they are attached; but

sometimes a number affects a group of symbols: thus, 3Mn.O. is three equivalents of protoxide of manganese $=Mn_3O_3$: thus, also, $S.O_3$ K.O.+Al_2O_3. $3S.O_3$, the formula of dry alum, contains four figures of 3, of which the first, second, and fourth only affect the O., to which they are subjoined, but the third affects the $S.O_3$, to which it is prefixed. A little practice will enable the student to become quite familiar with the arrangement of the symbols, or formulæ, as they are termed, of bodies, even of the most complicated nature.

This is the principle of multiple proportions: that the successive quantities in which one body may unite with another are multiples of the first by a whole number; and the cause of this is at once seen, and a simple and positive meaning given to this law, by saying that the first body contains an equivalent of each element; the second, one equivalent of one and two equivalents of the other, and so on; the successive steps being formed by the number of combining proportions of the second body which unite with one combining proportion of the first.

This principle, which establishes a remarkable distinction between the action of chemical affinity and of cohesion, was, at the moment of its first being traced, attacked by Berthollet, to whose exclusive doctrines it was quite fatal. Berthollet, in fact, considered that the affinity of bodies should make them unite in all possible proportions, and that it was only by the influence of cohesion and elasticity that the formation of the bodies actually produced resulted. Thus he asserted that sulphuric acid and barytes actually unite in all proportions; but those of 40·1 of acid to 76·7 of base forming the body of the least solubility, the whole quantity of acid is determined to unite with the barytes in those proportions, and in none others. Thus he imagined, also, that mercury and oxygen should unite in all proportions and that it was only by the intervention of external causes that their union was determined in preference to occur in the proportions of 101·4 of mercury to 4 of oxygen, and 101·4 of metal to eight of oxygen. We owe to Proust the complete refutation of Berthollet's views in this respect; he cleared away a heap of incorrect ideas which had prevailed regarding compound bodies, showing that numerous degrees of oxidation, which had been looked upon as intermediate, and connecting the extreme limits, as Berthollet thought they ought to be connected, were impure and badly prepared mixtures of the true compounds, and that, when pure, the transition from one state to the other is sudden and definite, as has been shown to be the consequence of the law of multiple proportion. It is interesting to notice, however, as an example of how easily a great discovery in science may be lost, that, although Proust had in his hand all materials necessary for establishing the laws of combination, such as they have been described, they escaped his notice, from his having contemplated his results only in one point of view; thus he found that in 100 parts,

1st Oxide of copper contained		2d Oxide of copper contained	
Oxygen	11·22	Oxygen	20·17
Copper	88·78	Copper	79·83
1st Oxide of mercury		2d Oxide of mercury	
Oxygen	3·80	Oxygen	7·32
Mercury	96·20	Mercury	92·68
1st Sulphuret of iron		2d Sulphuret of iron	
Sulphur	37·23	Sulphur	54·26
Iron	62·77	Iron	45·74

He proved that no indefinite intermediate degree of combination could be traced, and that the influence of cohesion could not be supposed to be the only cause of the definiteness of constitution; but, had he made a trifling change in his way of calculation; had he taken a certain weight of one element as the standard, and not 100 parts of the compound body, his numbers would have become,

1st Oxide of copper		2d Oxide of copper	
Oxygen	100·0	Oxygen	200·0
Copper	791·4	Copper	791·4

1st Oxide of mercury		2d Oxide of mercury	
Oxygen	100·0	Oxygen	200·0
Mercury	2531·6	Mercury	2531·6
1st Sulphuret of iron		2d Sulphuret of iron	
Sulphur	201·2	Sulphur	402·4
Iron	339·2	Iron	339·2

And thus the fact of the quantity of oxygen or sulphur in the second range of compounds, being exactly double that in each of the first, would have been evident and the law of multiple proportions been discovered twenty years before its existence was suspected.

We are now in a condition to examine more in detail the method of determining the equivalent number of a body, which, as was before noticed, is rendered difficult, sometimes, when the substances in question unite in more proportions than one. Thus it is evident that the manganese series might be represented as

100 of oxygen	+	345·9 of manganese,	forming		protoxide.
100	"	230·5	"	"	sesquioxide.
100	"	172·9	"	"	peroxide.
100	"	138·3	"	"	manganous acid.
100	"	115·3	"	"	manganic acid.
100	"	98·8	"	"	permanganic acid.

And the metallic oxides and sulphurets above described might be written, and express still the law of multiple proportion; as,

1st Oxide of copper		2d Oxide of copper	
Oxygen	100·0	Oxygen	100·0
Copper	791·4	Copper	395·7
1st Oxide of mercury		2d Oxide of mercury	
Oxygen	100·0	Oxygen	100·0
Mercury	2531·6	Mercury	1265·8
1st Sulphuret of iron		2d Sulphuret of iron	
Sulphur	201·2	Sulphur	201·2
Iron	339·2	Iron	169·6

There might thus be deduced from each kind of compound a different equivalent for each simple body, and it is therefore necessary to lay down some general principles by which one must be guided in their choice.

First. Whenever there exists but one proportion in which two bodies are capable of combining, it may be concluded, unless there are good reasons to the contrary, derived from other sources, that the proportion is one equivalent of each element. Thus lime and magnesia are the only compounds formed by the metals calcium and magnesium uniting with oxygen, and are hence looked upon as protoxides.

Second. Whenever one body combines with another in two proportions, as a metal with oxygen, and the quantities of oxygen are as 2 : 1, it may be concluded, unless there are other reasons for an opposite decision, that the bodies consist either of one equivalent of metal united respectively with one and two of oxygen, or of one equivalent of oxygen united respectively with one and two of metal. To decide between these views, it must be considered, that as the tendency of the metal and of oxygen to unite is pretty well satiated by the combination of an equivalent of each, if the protoxide so formed unite with another equivalent of either metal or of oxygen, this will be retained with inferior power, and when the substance so produced is exposed to decomposing agencies, it may be resolved

into protoxide and metal in the one case, and protoxide and free oxygen in the other. Thus copper, lead, and mercury unite each with oxygen in two proportions; and if black oxide of mercury be heated, it resolves itself easily into metallic mercury and red oxide, while the red oxide undergoes no change except total decomposition into mercury and free oxygen. Red oxide of copper decomposes itself easily into metallic copper and black oxide of copper; but this last does not admit of any decomposition which is not total. If we take yellow oxide of lead, we cannot change it by the application of heat; but if we heat brown oxide of lead, it gives off one half of its oxygen, and yellow oxide remains; similarly, when peroxide of manganese is heated by deoxidizing agents, it abandons one half of its oxygen, but the oxide so formed cannot be farther reduced. In this way, therefore, we conclude that

Red oxide of copper is suboxide. Cu_2O.
Black oxide of copper is protoxide. $Cu.O$.
Black oxide of mercury is suboxide. Hg_2O.
Red oxide of mercury is protoxide. $Hg.O$.
Yellow oxide of lead is protoxide. $Pb.O$.
Brown oxide of lead is deutoxide. $Pb.O_2$.
Olive oxide of manganese is protoxide. $Mn.O$.
Black oxide of manganese is deutoxide. $Mn.O_2$.

Thus, also, hydrogen and oxygen unite in two proportions, to form, in one, water, a body remarkably neutral in properties and permanent in constitution, and in the other oxygenated water, of which half of the oxygen is so loosely combined that its decomposition is provoked by the slightest causes, and is explosively violent. It is hence concluded that

Water is protoxide of hydrogen. $H.O$.
Oxygenated water is deutoxide. $H.O_2$.

If there be still more degrees of combination of the two bodies, these principles apply still more determinately to their characteristic properties.

Third. The constitution of an acid may be frequently determined by the consideration that an equivalent of it is the quantity which neutralizes an equivalent of a well-characterized base. Thus the equivalent number of potash on the hydrogen scale is 47·3, and this combining with 40·1 of sulphuric acid to form neutral sulphate of potash, this number is determined to be the equivalent of the acid; and as it is made up of 16·1 of sulphur and 24 of oxygen, the acid is considered to be composed of one equivalent of sulphur 16·1, and three equivalents of oxygen $8 \times 3 = 24$. Its formula is therefore $S.O_3$. In the same way, on analyzing hyposulphate of potash, it is found to consist of 47·3 of potash, united to 72·2 of the acid, which is, therefore, its equivalent number. But this number is made up of 32·2, or two equivalents of sulphur, and 40, or five equivalents of oxygen, and the formula expressing its constitution is S_2O_5.

Where an acid forms several classes of salts, it is difficult to determine which is that containing an equivalent of each element, and

hence this mode of ascertaining the constitution of the acid may be occasionally at fault. This happens particularly with the acids of phosphorus and arsenic; and in these cases it is necessary to recur to considerations regarding the constitution of their salts, which will be described when we come to speak of salts in general.

Fourth. In cases where the ratio between the quantities in which the bodies combine does not follow the simple proportion of 1 : 2 : 3, &c., but assumes the more complex form of 2 : 3, or 3 : 4, or 3 : 5 : 7, it is necessary to seek for analogies between the members of the series and certain other bodies with regard to which there is not the same uncertainty. Thus there are two oxides of iron which may be looked upon as consisting, either

the 1st of	27·9 of iron	+ 8	oxygen.
the 2d	27·9 "	+12	"
or the 2d	18·6 "	+ 8	"
the 1st	27·9 "	+ 8	"

In the first mode of view the oxygen varies as 2 : 3, but in the second it is the metal which changes in proportion. Here we obtain a guide in the study of the salts formed by these bodies. It is found that the oxide which contains 27·9 of iron to 8 of oxygen agrees in its laws and properties with magnesia, with black oxide of copper, and with olive oxide of manganese, which are all protoxides, and that it differs totally in its relations from such bodies as are very fully known to be suboxides. This oxide of iron contains, therefore, an equivalent of each element, and its formula is Fe.O. The peroxide of iron then becomes Fe.O $1\frac{1}{2}$; but as the equivalent of oxygen cannot be considered to be divided, we look upon it as being rather Fe_2O_3, and having its equivalent number twice as large. This view is confirmed by finding that when sulphate of peroxide of iron unites with sulphate of potash to form iron alum, it does so in the proportion of Fe_2O_3, dry iron alum being $S.O_3$, $K.O.+Fe_2O_3$, $3S.O_3$; and as this is the only proportion in which these two salts unite, it is reasonable to suppose that it contains an atom of each element.

This mode of controlling the equivalent numbers is beautifully shown in the instance of the compounds of chrome with oxygen. There are two; the

Green oxide of chrome consists of	18·79	chrome	+ 8	oxygen.
Chromic acid "	18·79	"	+16	"

Here the quantity of oxygen is doubled in the second compound; and as this yields half of its oxygen readily, either by heat, or to any substance having an affinity for it, it would appear highly probable that the 18·79 is the equivalent of chrome, and that the oxide of chrome should be looked upon as a protoxide; but such is not the case. Sulphate of chrome combines with sulphate of potash to form a chrome alum, resembling in all characters and constitution the iron alum already noticed, and hence oxide of chrome corresponds to peroxide of iron, and its formula is Cr_2O_3. This is farther proved by the relations of chromic acid to bases. The chromates resemble perfectly the sulphates with which they are isomorphous, and to saturate 47·3 of potash 52·2 of chromic acid are required, consisting

of 28·2 of chrome and 24 of oxygen; and hence the formula of chromic acid is $Cr.O_3$, resembling that of sulphuric acid $S.O_3$.

Fifth. In cases where there is only one compound of a body with oxygen, we may be induced to consider it not to be composed of an equivalent of each element from analogical grounds, such as those now described. Thus aluminum and oxygen form only one compound, alumina; but this resembles, in all its laws of combination and crystalline form, oxide of chrome and peroxide of iron, and hence it is considered to be a compound of two equivalents of metal and three of oxygen, and its formula to be Al_2O_3.

Sixth. When bodies are found combined in proportions expressed by high numbers, they are generally looked upon as secondary compounds, formed by the reunion of others, the ratio of whose elements are simple. Thus lead forms with oxygen compounds intermediate to the two true oxides already described, the one containing three equivalents of lead and four of oxygen, the other four of lead and five of oxygen; these consist really of the protoxide and peroxide united in the proportions shown by the equations:

$$Pb_4O_5 = 3Pb.O. + Pb.O_2, \text{ and } Pb_3O_4 = 2Pb.O. + Pb.O_2.$$

In like manner, between the two proper oxides of iron there intervene the two magnetic oxides, the formulæ of which are Fe_4O_5 and Fe_3O_4, being compounds of protoxide and peroxide, as,

$$Fe_4O_5 = 2Fe.O. + Fe_2O_3, \text{ and } Fe_3O_4 = Fe.O. + Fe_2O_3.$$

By this means the constitution of an extensive class of complex bodies is reduced to very simple forms.

If we take oxygen, hydrogen, chlorine, and nitrogen in the proportions by weight which correspond to their equivalent numbers, and measure the volumes which, as gases, they occupy, an exceedingly striking relation will be found between them, the volume of oxygen being exactly one half that of each of the other gases. If, also, we heat iodine and bromine in quantities proportional to their equivalents by weight, we shall find that, when converted into vapour, they occupy precisely the same volume as the equivalent of hydrogen gas at the same temperature and pressure. On converting into gas equivalent weights of arsenic and phosphorus, they occupy precisely the same volume, which is equal to that of the equivalent of oxygen gas; and by similarly treating an equivalent of sulphur, its volume becomes one third that of the oxygen. Finally, when a quantity of mercury, representing its equivalent number, is converted into vapour, its volume, reduced to the same standard of temperature and pressure, is four times that of oxygen, and double that of hydrogen or chlorine gases. It hence results, that although the equivalent weights of the simple bodies may be totally unconnected, and may range within very extensive limits, yet the volumes which these equivalent quantities occupy when in the state of gas or vapour, have a very simple relation to one another; thus, taking the equivalent weight of oxygen as 100, and its equivalent volume as 1, the proportion of the other bodies mentioned are:

Name of Substance.	Equivalent Weight.	Equivalent Volume.	Sp. Gr. of Vapour. Air=1000.
Oxygen . .	100·0	1	1102·6
Hydrogen . .	12·5	2	68·8
Chlorine . .	442·6	2	2470·0
Iodine . . .	1579·5	2	8701·0
Bromine . .	978·3	2	5393·0
Nitrogen . .	175·0	2	976·0
Sulphur . .	201·2	$\frac{1}{3}$	6648·0
Phosphorus .	392·3	1	4327·0
Arsenic . .	940·1	1	10362·0
Mercury . .	1265·8	4	6969·0

Not merely does this simple proportion of equivalent volumes hold among the simple bodies, but it determines in the compounds which they form an equally regular constitution.

The volumes of the gases which unite are necessarily in simple equivalent proportion to each other, and when the same gases unite in more than one proportion, the second is a multiple of the first. In all cases, also, where, after union, a condensation of volume occurs, the resulting volume is simply related to the volumes which the constituents had occupied before combination. Thus, in the formation of water, one volume of oxygen unites with exactly two of hydrogen, and the volume of watery vapour which is formed is equal to that of the hydrogen employed. To form ammonia, one volume of nitrogen unites with three of hydrogen, and the four volumes are condensed into two by the combination. There may, therefore, be arranged for the various bodies which assume the gaseous form, a series of equivalents in volume, which will not be totally unconnected numbers, like those of the equivalents by weight, but are found to be, as the weights should become if the suggestion of Proust were verified, simple multiples of the equivalent of some standard body which may be selected, as oxygen in the table.

Name of the Compound Vapour.	Formula.	Equivalent Weight.	Equivalent Volume of Constituents.	Equivalent Volume of Compound.	Sp. Gr. of the Vapour. Air=1000·0.
Water	H.O.	112·5	3	2	620·2
Nitrous oxide	N.O.	275·0	3	2	1527·3
Nitric oxide	$N.O_2$	375·0	4	4	1039·3
Sulphurous acid	$S.O_2$	401·2	7	6	2210·6
Sulphuric acid	$S.O_3$	501·2	10	6	2761·9
Sulphuretted hydrogen . . .	S.H.	213·7	7	6	1177·0
Muriatic acid	Cl.H.	455·1	4	4	1269·5
Hydriodic acid	I.H.	1592·0	4	4	4385·0
Hydrobromic acid	Br.H.	990·8	4	4	2731·0
Ammonia	$N.H_3$	214·5	4	4	591·5
Arseniuretted hydrogen . . .	$As.H_3$	952·6	7	4	2694·0
Terchloride of arsenic . . .	$As.Cl_3$	2268·0	7	4	6295·0
Calomel	$Hg_2Cl.$	2974·3	6	4	8204·0
Corrosive sublimate	Hg.Cl.	1708·5	8	4	9439·0
Arsenious acid	$As.O_3$	1240·1	4	1	13670·0
Sulphuret of mercury . . .	Hg.S.	1467·0	7	9	5384·0
Chloride of sulphur	$S_2Cl.$	845·0	4	3	4686·0
Protochloride of phosphorus .	$P.Cl^3$	1720·1	7	4	4741·1
Perchloride of phosphorus . .	$P.Cl_5$	2505·3	11	6	4788·1

The simplicity thus shown to exist between the volumes of the constituent and compound vapour enables us very often to calculate beforehand what the specific gravity of a vapour should be, and thus

to ascertain how closely the numbers found experimentally by the methods described in the first chapter may approach to absolute correctness. Thus, to calculate the specific gravity of ammonia: it is formed by the union of three volumes of hydrogen and one of nitrogen, and the weights of these volumes being as their specific gravities, the weight of the ammonia formed should be $976+(3\times 69)=1183$ if the four volumes of constituents were condensed into one; but as the condensation is into two, the specific gravity of the ammonia is $1183\div 2=591{\cdot}5$, as given in the table. Sulphur and hydrogen unite in the proportion of one volume of sulphur to six of hydrogen, and hence, if there were but one volume of resulting gas, the specific gravity should be $6648+(6\times 69)=7062$; but as there are six volumes of gas formed, the true specific gravity of sulphuretted hydrogen is $7062\div 6=1177$. The general rule being to multiply the specific gravities of the simple gases or vapours respectively by the volumes in which they combine, to add those products together, and then to divide the sum by the number of volumes of the compound gas produced.

By the application of this principle, we may often decide with great probability on the specific gravity which certain bodies should have in the state of vapour, although it has not been as yet possible to weigh their vapours experimentally. Thus the temperature at which antimony is volatile is so high that the specific gravity of its vapour may possibly never be determined by experiment; but the chloride of antimony resembles, in all its chemical relations, chloride of arsenic, and there is the greatest probability that the constitution of the two are alike in the state of vapour. Now we know that chloride of arsenic consists of six volumes of chlorine and one volume of arsenic vapour condensed into four volumes; and hence, if we multiply the specific gravity of the vapour of chloride of antimony, which is 8106·5, by four, we obtain 32426·0, and subtracting from it the weight of six volumes of chlorine $=14820$, there remains 17606, which, if the analogy between the arsenic and antimony be correct, must be the specific gravity of the vapour of antimony reduced to the standard of air $=1000$.

Similar principles have been applied to the determination of the specific gravity which carbon should possess if it were converted into vapour. This number would be of great importance in all calculations of the specific gravities of the vapours of organic bodies, most of which contain carbon as an element; but, unfortunately, there is no volatile body so similar to carbon as that its analogies can be taken as a guide, and hence the bases of the calculated density of gaseous carbon are purely hypothetical. Indeed, chemists are not agreed upon the precise number, some making it the double of what it is estimated at by others. If we look upon carbonic acid as consisting of equal volumes of vapour of carbon and oxygen, the two condensed into one, the specific gravity of carbon is $1524{\cdot}1-1102{\cdot}6=421{\cdot}5$; but if the carbonic acid consist of two volumes of oxygen and one of carbon, the three volumes condensed into two, the calculated specific gravity of the latter vapour is $3048{\cdot}2-2205{\cdot}2=843{\cdot}0$. On the first idea, the carbonic oxide consists of two volumes of carbon vapour and one of oxygen, the three

condensed to two $(2\times 421{\cdot}5 + 1102{\cdot}6) \div 2 = 972{\cdot}8$; and on the latter, of equal volumes united without condensation $(843{\cdot}0 + 1102{\cdot}6) \div 2 = 972{\cdot}8$. It is this latter view which I adopt, and in any calculations that may occur hereafter, I shall consider the specific gravity of gaseous carbon as 843. It does not at all necessarily follow that the true specific gravity is either of these numbers, as it may be that the relations by volume of carbonic acid and carbonic oxide are much more complex. Before the specific gravity of the vapour of sulphur had been experimentally determined, it was considered, from similar theoretic grounds, to be 2216, but it is actually three times as great, 6648, and we must hence not reckon too implicitly on the relations by volume at present given for the gaseous compounds of carbon.

In the combination by volume, the same laws of multiple proportion hold as in combination by equivalents; thus the compounds of chlorine and oxygen, which are by weight Cl. O., $Cl.O_4$, $Cl.\ O_5$, and $Cl.\ O_7$, are by volume two of chlorine to one, to four, to five, and to seven volumes of oxygen respectively, and so in all other instances; and, consequently, all remarks that have been made regarding the law of multiple proportions in equivalents by weight, apply to combinations of equivalents by volume also.

CHAPTER X.

OF THE RELATIONS OF CHEMICAL CONSTITUTION TO THE MOLECULAR STRUCTURE OF BODIES.

It has been abundantly shown, throughout the preceding portions of this work, that even the most purely physical properties of a body are closely connected with its chemical constitution; and that thus the density, the crystalline structure, or the electrical relations of a substance, or the manner in which it is acted on by heat, may, by affording distinctive characters, or by influencing its affinities, become necessary to its chemical history. The numerical laws of constitution last described yield additional evidence of the intimate relation of chemical to molecular constitution; and in the present chapter I purpose to conclude the description of the general history of chemical action, by an account of such principles as have been advanced, and such facts as have been discovered illustrative of this connexion. They are as follow:

1st. The connexion between the molecular constitution and the equivalent numbers of bodies. *The atomic theory.*

2d. The connexion between the crystalline form and the chemical equivalency of bodies. *Isomorphism.*

3d. The relation of constitution to composition. *Of Dimorphism and Isomerism. The theory of types.*

4th. Of chemical action independent of affinity. *Catalysis.*

SECTION I.

OF THE ATOMIC THEORY.

It was natural that, as soon as the remarkable laws of combination discussed in the last chapter had been discovered, philosophers should be anxious to ascend to the causes in which they had their rise, and to trace, in the operation of some one general principle, the three determinate numerical conditions to which experiment proved chemical action to be subjected; accordingly, such theoretical views were promulgated even before the laws of combination were fully understood; and it has been since one of the most difficult tasks of the philosophic chemist to disentangle the real and practical from the merely speculative portions of atomic chemistry.

For Dalton, in promulgating the law of multiple combination, the most beautiful, as well as the most extensive principle that had been conferred on chemistry since the epoch of Lavoisier, announced it as the result of speculations which, though in their general nature true, and constituting still the essential basis of all theories of chemical action, were yet overlaid by a tissue of hypotheses so irregular and so unnecessary, that for a long time the real dignity and excellence of the experimental laws were underrated and misunderstood. These accessory speculations have now, however, passed away, and the theory of combination laid down by Dalton may, in all its essential conditions, be very briefly expressed as follows:

All substances are supposed to be constituted of particles perfectly indivisible, and hence truly *atoms*. In different kinds of matter, these atoms are of different weights, and probably of different magnitudes; but this latter quality is of no material interest. When bodies combine chemically, their combination must be so effected that one atom of one unites with one atom of another; or one of the first with two, or three, or four of the second; or two of the first with three, or five, or seven of the second; but no intermediate degrees can possibly occur, for the atom being absolutely indivisible, no intermediate degree of union can take place. The relative weights of these atoms are the equivalent numbers of the bodies combined; eight parts of oxygen unite with one part of hydrogen, by weight, to form water, because the simplest proportions in which they can unite are one atom of each, and the atom of oxygen is eight times as heavy as the atom of hydrogen; eight parts of oxygen are equivalent to 35·4 parts of chlorine, because, when an atom of hydrogen leaves the atom of oxygen, it combines with an atom of chlorine in its place, which is heavier than that of oxygen in the proportion of 35·4 to 8, and the quantity must be consequently so determined. When a second atom of oxygen combines with hydrogen, it being equally heavy with the first, doubles the quantity of oxygen which the equivalent of hydrogen has taken up, and, as might be illustrated by any series of examples, introduces as a necessary consequence the law of multiple combination.

Such is the atomic theory of Dalton. It expresses faithfully the laws of combination; 1st, the law of definite constitution; 2d, the principle of equivalent proportion; and, 3d, the law of multiple com-

bination. It is therefore, even in this form, the most embracing and perfect generalization that has ever been proposed in chemistry; but, before committing ourselves implicitly to its adoption, it is necessary to examine into its bases with some detail.

Dalton assumes that matter is constituted of indefinitely small particles, *atoms*, but he advances no proof that it is so; he adopts, unreservedly, that side of the discussion which, from the earliest ages, has divided the opinions of philosophers, and shows that on that hypothesis all the most remarkable phenomena of chemistry can be explained. But I have already, in the first chapter of this work, pointed out, that the question of the ultimate constitution of matter is now no nearer its solution than it was twenty centuries ago; and I will now proceed to show, that for the explanation of the laws of combination, the atomic theory of Dalton is unnecessary, or, at least, that it becomes only one out of a variety of molecular conditions which matter may assume. In the first place, it is necessary to ascertain in what manner the relative weights of the atoms of bodies, if they really exist, are to be determined.

I pointed out in the last chapter the number of circumstances which should be taken into account for the determination of the equivalent number of a body; it is by such considerations that in similar cases the atomic weight of a body is determined; and where the idea of the existence of such ultimate combining molecules is adopted, the atom is the equivalent, and the number is its weight. If, therefore, the theory of molecular constitution involved chemical results alone, no difficulty would occur; but when we consider these atoms as building up the mass, and conferring upon it its physical properties at the same time that they produce its chemical constitution, inconsistencies are found which must prevent our coming too hastily to a conclusion.

When Gay Lussac first determined the existence of those simple relations which have been described as existing between the volumes of gases which combine together, it was considered certain that all gases contained in the same volume the same number of atoms. The gases are remarkable for all possessing the same physical constitution. Their relations to pressure and to heat are governed by the same law in all cases, which can be best explained by supposing that in the same space they contain the same number of ponderable atoms, set at equal distances from each other, and whose material repulsion is expressed by the same law. Hence, when one volume of chlorine unites with one of hydrogen, an equal number of atoms of each element come into play, and an atom of the compound consists of an atom of each constituent. But here a difficulty occurs; the chloride of hydrogen which results occupies two volumes, and yet it is in physical properties identical with the hydrogen or chlorine; all physical evidence would lead us to believe that muriatic acid gas contained in the same volume the same number of atoms as its constituents, but the most positive chemical evidence shows that it contains but half so many. In like manner, on physical grounds, there should be the same number of atoms in the same volume of oxygen and hydrogen; and as water is formed by the union of one volume of oxygen with two of hydrogen, it should

consist of one atom of oxygen and two atoms of hydrogen; but the most perfect chemical evidence we possess proves that water is composed of an equivalent of each element. The number of chemical molecules in gases is different, therefore, for each gas; it is the combining or equivalent volume which contains equal numbers of chemically equivalent molecules or atoms, and, as has been shown in the tables in the last chapter, those volumes differ remarkably from one gas to another.

Another physical condition, which is intimately connected with the molecular constitution and the chemical relations of bodies, is their specific heats, on the remarkable law of which, regarding the simple bodies, as discovered by Dulong and Petit, and extended to many compound bodies by Nauman and Avogadro, I have already fixed attention (page 67). If we look upon the specific heats of all the ultimate particles of simple bodies as being the same, we should at once have a mode of determining their atomic weights, and these should coincide with the equivalents deduced from chemical considerations.

In the great majority of cases, the atomic weights of the solid simple bodies, deduced from their specific heats, coincide with those adopted from chemical considerations; and in some of the exceptional instances, as bismuth and silver, there is doubt as to the true number, which may be fairly interpreted as so far remaining neutral. But in other cases we find that it completely fails; thus, the atomic weight of iodine, deduced from its specific heat, is 63·1, while there is no doubt but that its chemical equivalent is 126·3, twice as much. Also, the history of arsenic and phosphorus is so complete, that there is no doubt that their equivalents are 75·4 and 31·4; but when we calculate the atomic weights from their specific heats, we find as the result for arsenic 37·7, and for phosphorus 15·7, that is, in each case but the half of the real number. In the gases, also, there is complete discordance between the specific heats and the chemical equivalents, no matter whether we consider their purely molecular constitution, by which they should have an equal number of atoms and equal specific heats in equal volumes, or whether we compare their combining volumes with their specific heats. The specific heats of equal volumes (p. 69) of oxygen and of hydrogen have been proved by Apjohn to be as 808 to 1459, while on chemical grounds that of oxygen should be double, and on molecular considerations the same as that of the hydrogen.

It follows, from what has been said, that it is totally impossible to adopt completely the opinion of Dalton, that bodies are composed of ultimate and indivisible particles, which, aggregating together, give origin to sensible masses of the same nature when similar particles unite, and to the phenomena of chemical combination when the union is between particles of different kinds; I adopt fully the idea of Dumas, that it is possible, and, indeed, more consonant to experiment, to explain all the laws of chemical combination quite independent of all considerations as to whether the masses which combine are indivisible or the reverse. The word *atom*, if interpreted in its strict and proper sense, is unnecessary, and may be injurious if employed with any vague or undefined meaning.

I consider, as I have already stated (page 17), that sensible masses of matter are constituted of a number of lesser masses, which again may be made up of similar constituent groups, proceeding downward to any extent, but still without involving the question of a limit to the degree of possible division. One class of these groups of particles I consider to be represented by the equivalent numbers; and it is possible that these numbers may indicate the manner in which the chemically combining groups may be supposed to subdivide themselves, in order to generate a set of groups of an inferior class. The specific heats of bodies may be considered to have reference to an order of groups of particles often, but not necessarily, coincident with those which combine to produce chemical compounds; and the third, probably the most remote, engaged in the ordinary properties of matter, may be such as, being uniformly distributed in the gaseous form, confers upon those bodies the properties which characterize mechanically that condition, and are independent alike of the chemical properties and specific heats which appertain to, and are exhibited by, groups of a more complex structure and superior order.

From this point of view I contemplate the atomic theory; for these groups, engaged in chemical combination, and indivisible by chemical means, are, in all chemical relations, *atoms*. Their relative weights are our equivalent numbers. From their union the laws of definite and multiple combination directly follow. But, when we remove them from their proper sphere, when we subject them to physical forces, we may dissect them, and separate them into other groups; or we may unite many of them together to form a larger group, characterized by the relations to heat and to pressure that have been already stated, but no longer the group or atom engaged in chemical operations. Thus the group which is acted on by the heat when a gas expands, occupies only half the space in muriatic acid that the chemical group takes up; but in gaseous sulphur it occupies three times the space of the chemical atom. In gaseous oxygen, arsenic, and phosphorus, the mechanical atom is of the same volume, but the chemical atom only of half the volume that they respectively occupy in hydrogen, chlorine, and iodine. In most of the simple bodies the same groups produce chemical combination, and determine the specific heat; but in iodine, in arsenic, and in phosphorus, the group which enters into chemical combination contains two of the groups which are pointed out from the specific heats of these bodies.

I shall frequently employ the word *atom* in the course of the following pages, but I do so only as an abbreviation for the terms *equivalent quantity* or *combining masses*. Of the ultimate particles of matter, or true *atoms*, we know nothing; and all of the discussions that have taken place, from the earliest and vaguest speculations of Democritus or Leucippus, to the modern experiments of Wollaston and Faraday, must be considered as absolutely without influence on the positive decision of the question.

SECTION II.

OF ISOMORPHISM.

The general principles of the isomorphism of crystallized substances have been already noticed, with relation to the fact of their substitution for each other (page 31), and of the advantage with which this property may be applied to determine equivalent numbers (page 212); it now remains to study this character, as indicative of the molecular constitution of the body.

It must, in the first place, be carefully observed, that identity of crystalline form does not imply similar chemical constitution, unless under limiting circumstances, which require to be studied with great care. The principle upon which all subsequent reasoning must rest is, that in proportion as the structure of the crystal becomes more complex, and the conditions necessary for its formation, consequently, more varied, the greater probability is there that two bodies shall not assume exactly the same form, unless their chemical constitution and the molecular arrangement belonging to it be the same, or, at least, similar in both. Hence, in the regular system, there can be no inference whatsoever drawn with regard to constitution from the crystalline form alone. Bodies the most contrasted possible in their properties and composition have identical external figures, as fluor spar, bismuth, alum, sulphuret of lead, common salt. The conditions of molecular arrangement for the forms belonging to this system being the easiest possible to fulfil, the greatest variety in the number and grouping of the chemical constituents is allowable.

In the other systems of crystallization, where the double refraction and the rings produced by polarized light, transmitted along their principal axis, indicate a much greater complexity of structure, it becomes highly improbable that the molecules of two bodies shall be so similar to each other as to produce identity of crystalline form, unless there is, if the body be compound, a similarity of composition, or, if the body be simple, such similarity of properties as brings the two into the same group in a natural classification. This probability increases with the complexity of molecular structure of the crystals.

The isomorphism of compound bodies has been explained upon the supposition that, in such cases, the replacing elements were themselves isomorphous, and hence might change places without disturbing the mechanical arrangement of the other components of the crystal. Thus, in the sulphuric, chromic, selenic, telluric, and manganic acids, which contain each three equivalents of oxygen, the molecules of sulphur, chrome, tellurium, selenium, and manganese have all the same form. The perfect determination of whether those elements are really thus isomorphous, is very difficult, from the fact of comparatively very few being crystallizable. Thus tellurium and sulphur are those of which, alone, we know the crystalline form, for the only crystals of selenium that have been observed are microscopic and imperfect, and neither chrome nor manganese can be had crystallized at all. We must, therefore, be guided

by analogy in such cases; and if we examine another group of compounds into which chrome and manganese enter, we find that Cr_2O_3 and Mn_2O_3 are isomorphous with Fe_2O_3, and Mn.O. and Fe.O. are isomorphous with Cu.O. Now we here arrive, by a chain of isomorphous conditions, at a metal which may be obtained crystallized, but the crystalline form of copper is always one of the regular system, as the cube, octohedron, rhombohedron, dodecahedron, &c.; while sulphur, with which it should be isomorphous, if this principle were absolutely true, crystallizes in two forms, of which one belongs to the oblique prismatic, and the other to the right prismatic system; while tellurium belongs to the rhombohedral system, affecting a totally different form altogether. Numerous other instances might be taken; thus the periodic, perchloric, and permanganic acids are isomorphous ($I.O_7$, $Cl.O_7$, and Mn_2O_7), while the elements themselves are certainly not necessarily isomorphous, as iodine belongs to the right prismatic system. Also the isomorphism of the phosphoric and arsenic acids ($P.O_5$ and $As.O_5$) is one of the best examples that has been found; but phosphorus and arsenic are so far from being isomorphous, that phosphorus crystallizes in the regular, and arsenic in the rhombohedral system. The principle that compound bodies are isomorphous, because their replacing elements have necessarily the same figure, is therefore one which cannot be received in science.

Another idea suggested for the explanation of the phenomena of isomorphism is, that the crystalline form of a body is completely independent of its chemical composition, and is produced only by the number of ultimate particles or atoms by which it is made up. Thus alum has the same form, whether it contains aluminum or iron, or manganese or chrome, not because their particles have the same figure, but because, in all these cases, the molecule of alum is made up of the same number (71) of simple atoms. This idea is, however, even less tenable than the former; for it supposes that we have arrived at the ultimately simple bodies, the true elements, which is a very unphilosophical assumption; and according to it, bodies could replace each other only when they were all simple or all of the same degree of composition, which is not the case; and also among the simple bodies, that the replacement should be always by an equal number of ultimate molecules, which is also negatived by experiment. Thus we find that an equivalent of a simple body, K., is replaced by a group of five equivalents, $N.H_4$, and that the simple atom, Cl., is replaced by the two atoms Mn_2. This suggestion cannot, therefore, be considered as satisfactory, and we must examine farther into the conditions of isomorphous replacement before we attempt the farther discussion of the source from whence it has its rise.

It is necessary first to study the crystalline relations of the unde composed bodies, both so far as they have been really observed, and as they generate similar compounds which are isomorphous. The simple bodies which are known to crystallize are:

Regular System.	*Rhombohedral.*
Carbon.	Carbon.
Phosphorus.	Tellurium.
Selenium.	Arsenic.
Copper.	Antimony.
Silver.	
Gold.	*Right Prismatic.*
Platinum.	Sulphur.
Mercury.	Iodine.
Bismuth.	
Titanium.	*Oblique Prismatic.*
Lead.	Sulphur.

It is thus seen that, of the simple bodies which may be obtained crystallized, two thirds crystallize in the regular system, which, as already noticed, prevents our resting upon their forms any chemical reasoning; and the bodies whose isomorphous equivalency is best established, are not found to belong even to the same system. Carbon and sulphur are known also to have each two forms of different systems, and to be thus dimorphous. It must be observed, however, that the assumption of the forms of the regular system by so many of the simple bodies, particularly among the metals, may arise from circumstances such as confer the external cubical figure on analcime or boracite, and that their internal structure may be, in reality, more complex, and their arrangement different; for the metals do not reflect light as other bodies of the regular system do; they change it into the state of elliptical polarization; and in the only case where light can be examined, after having been refracted through a metal, that of gold leaf, it is found to be elliptically polarized also. The diamond resembles the metals in this property, and is found sometimes to possess double refraction, which should belong also to the metals, probably, if their nature allowed it to be tried. The cubic crystals of gold, copper, and bismuth, the octohedrons of lead, silver, and zinc, may therefore belong to the square or right prismatic systems, the three axes being equal among each other, and hence the isomorphism of the simple bodies be rendered still less probable.

The examples of isomorphism in compound bodies, which are most deserving of attention, are the following:

GROUP I.

Sulphuric acid	$S.O_3$	These acids, the composition of which is similar in all, form salts, which, when they contain the same base, and the same proportion of base and of water of crystallization, have the same crystalline form.
Telluric acid	$Te.O_3$	
Selenic acid	$Se.O_3$	
Chromic acid	$Cr.O_3$	
Manganic acid	$Mn.O_3$	

GROUP II.

Magnesia	Mg.O.	These protoxides combine with acids and form salts, which, when in the same degree of saturation with base and water of crystallization, have the same form. The sulphates of these oxides combine with sulphate of potash to form isomorphous double salts.
Protoxide of iron	Fe.O.	
Protoxide of manganese	Mn.O.	
Oxide of copper	Cu.O.	
Protoxide of cobalt	Co.O.	
Protoxide of nickel	Ni.O.	
Oxide of zinc	Zn.O.	
Oxide of cadmium	Cd.O.	

GROUP III.

Sesquioxide of iron . . . . Fe_2O_3
Sesquioxide of manganese . . Mn_2O_3
Oxide of chrome . . . . Cr_2O_3
Alumina . . . . Al_2O_3
These sesquioxides, combined with sulphuric acid, with sulphate of potash, and with water, form the different species of alum, which have all the octohedral form. They are themselves also isomorphous.

GROUP IV.

Potash . . . . $K.O.$
Soda . . . . $Na.O.$
Hydrated ammonia . . . . $N.H_3H.O.$
Hydrate of lime . . . . . $Ca.O.H.O.$
These fixed alkalies may be substituted for each other in the different species of alum. The hydrated ammonia, $H.O.N.H_3$ (often called oxide of ammonium, $N.H_4O.$), is truly isomorphous with potash in all its compounds; but it is only rarely that the compounds containing soda appear to have the same form. In minerals, and in some forms of alums, potash is replaced by an atom of any oxide in Group II., united with an atom of water, as hydrate of lime, or by two atoms of such compound without water.

GROUP V.

Phosphoric acid . . . . . . $P.O_5$
Arsenic acid . . . . $As.O_5$
These acids combine with bases in different proportions to form each three classes of salts, between which respectively the isomorphism is complete. It was by the study of the forms of the corresponding arseniates and phosphates that Mitscherlich first established the principle of isomorphism, although the true laws of their constitution escaped his notice, and were only brought into view by the later excellent researches of Graham. Even now there is no example of isomorphism between two complete series of compounds so well established as that of the arseniates and phosphates.

GROUP VI.

Perchloric acid . . . . . . $Cl.O_7$
Permanganic acid . . . . . Mn_2O_7
Periodic acid . . . . $I.O_7$
The corresponding salts of these acids are truly isomorphous, and this group affords an example of a form to which I shall recur, that of one equivalent of one body being replaced by two of another, as Cl. by Mn_2.

GROUP VII.

Sulphuret of antimony . . . . $Sb.S_3$
Sulphuret of arsenic . . . . . $As.S_3$
Sulphuret of bismuth . . . . Bi_2S_3
These bodies, which are found crystallized in nature, have the same form. The oxide of antimony and the arsenious acid, $Sb.O_3$ and $As.O_3$, though they are not found crystallized in the same form, appear to replace each other in some salts without changing its figure, and may, therefore, be sometimes isomorphous.

GROUP VIII.

Stannic acid . . . . $Sn.O_2$
Titanic acid . . . . $Ti.O_2$
These are found native crystallized in the same form.

There are many other cases in which similarity of crystalline form has been observed between bodies of more or less analogous constitution; but as here I wish to bring forward only a sufficient number of the most remarkable examples of the principle, I shall postpone for the present the consideration of the remainder.

The principle of isomorphism, as thus described, has been supposed to require that the angles of the crystals of the isomorphous bodies should be truly equal, which they are not found really to be, for even in the best examples taken slight differences appear. Thus, in the carbonates of lime and magnesia, the angles of the rhombs differ by 2° 36′; in the sulphates of zinc and magnesia they differ by 38′; in the sulphates of barytes and strontia the difference is 2° 48′. To express this, the word *plesiomorphism*, indicating that such crystals are not exactly, but nearly, of the same form, has been proposed; but it is totally useless, as absolutely isomorphous forms would then be extremely rare. It is easy to understand that slight

changes in external circumstances might prevent the absolute isomorphism of two bodies, particularly as it is found that the value of the angles in different specimens of even the same substance is liable to fluctuation even to nearly a degree. I apprehend that we must seek the cause of these plesiomorphic differences in the peculiar circumstances under which the body forms, particularly with regard to temperature; for when a crystallized body, not of the regular system, is heated or cooled, it expands in different degrees, according to the direction of its axis, and may even contract in one direction while it is expanding in another; thus, when carbonate of lime is heated from 32° to 212°, the linear expansion in the direction of the principal axis is 0·001961, while in the direction of each horizontal axis a contraction of 0·00056 occurs; in consequence of this, the obtuse angle of the rhomb, which at 50° Fah. is equal to 105° 4′, becomes more acute by $8\frac{1}{3}$′, and the acute angles, which are 74° 54′ 15″, become more obtuse in a corresponding degree. Hence, if we heated or cooled, through a certain range of temperature, the various crystallized bodies of that group, they might be brought to coincide absolutely in form, and possibly, when at first generated, they were thus coincident; but by change of figure, when brought to ordinary temperatures, the small plesiomorphic differences may have occurred.

Isomorphism, considered as thus sketched, affords to the chemist the most valuable criterion at present at his disposal for determining those substances which replace each other most truly in combination; and where a number of bodies are so connected by external form, very important conclusions may be obtained as to the internal arrangement of their constituents. In this manner it has been satisfactorily established, that bodies may replace each other in proportions quite different from their ordinary equivalents, and thus pass, as it were, by a doubling or trebling of their atomic weights, into a different natural group; and that even two bodies, combined in an equivalent of each, may form a complex group, capable of being substituted for one of simpler structure. Thus an equivalent of chlorine is replaced by two equivalents of manganese; an equivalent of silver is replaced by two equivalents of copper; an equivalent of soda or of potash is replaced by two equivalents of lime, or of one of lime and one of water, or by one of lime and one of oxide of manganese or of iron, or by ammonia and water united to each other, or to an equivalent of a protoxide of the magnesian group. By such observations we obtain the foundations of a philosophical classification of bodies, with which the analogies drawn from purely chemical characters are found remarkably to correspond.

But it is important to ascertain whether the isomorphism of various bodies establishes necessarily, or even probably, in the absence of other reasons, grounds for assimilating the formulæ of the bodies, or imagining that their chemical constituents are equivalent and are arranged in the same way. This is a point which has been, as I consider, much misunderstood, and has led to some error and confusion. Thus anhydrous sulphate of soda crystallizes in the same form as perchlorate of barytes and permanganate of barytes; and if it be necessary, as a consequence of isomorphism, that these bodies should have similar constitutions, we must change the formula, $S.O_3$. Na.O. into S_2O_7 . Na_2O., in order to make it resemble Mn_2O_7 . Ba.O. This requires us to compare the sulphates whose elements are most pow-

erfully united, with some of the most easily decomposed salts that we know; it requires us to consider the alkalies as being suboxides, which is opposed by every circumstance in their history; and it requires us to consider two equivalents of sodium as being equivalent to one of barium, for which no other evidence can be had from other examples. But, again, the anhydrous sulphate of soda is isomorphous with sulphate of silver, and hence the formula of this last should be S_2O_7 . Ag_2O., which is so totally unsupported by other evidence that it has been proposed to subdivide the atomic weight of silver and sodium, for the purpose of explaining the isomorphism of Cu_2 and Ag. These examples are sufficient to show how unphilosophical is the attempt at rashly inverting the principle of isomorphism, and seeking to deduce, as a necessary consequence of the mere similarity of form, similarity of chemical constitution. Bodies of similar chemical constitution affect the same crystalline form; but bodies of the most diverse natures may have the same crystalline form also. Even without speaking of the regular system, where fluor spar and alum, Ca.F. and K.O. . $S.O_3$+Al_2O_3 . $3S.O_3$+24H.O., have the same form, we find numerous examples of this fact; nitrate of soda and carbonate of lime are isomorphous in the rhombohedral system, and nitrate of potash and carbonate of lead in the right prismatic system; the chemical constitution of the formulæ $N.O_5$. Na.O., and $C.O_2$. Ca.O., and that of the formulæ $N.O_5$. K.O., and $C.O_2$. Pb.O., are widely different, but the forces by which the assumption of crystalline form is governed are alike. Even in these instances the attempts at generalizing the chemical formulæ have been tried, and the nitrates of soda and potash have been written $N.O_6$ K. and $N.O_6$. Na., with which the formulæ of the carbonates, when doubled, $C_2O_6Ca_2$ and $C_2O_6Ba_2$, have been compared. In this way one equivalent of soda is made isomorphous with two of barytes, while by a former and similar reasoning, one of barytes was made isomorphous with two of soda. Bisulphate of potash, K.O. . $S.O_3$+H.O. . $S.O_3$, crystallizes in two forms, one of which is that of sulphur, a simple body, and the other of which is that of feldspar, K.O. . S_3+Al_2O_3 . $3So_3$. Here, in neither case is there the slightest similarity of constitution.

The circumstances of isomorphous replacement may be reduced to the following simple propositions, with which I shall terminate the subject:

1st. Similarity of crystalline form requires that the molecular structure of the bodies shall be alike, but has no necessary reference to the chemical nature or composition of these molecules. Examples.—Nitrate of soda and carbonate of lime, sulphate of soda and perchlorate of barytes, bisulphate of potash and sulphur.

2d. When the physical molecules consist of chemical elements which follow the same laws of combination, and which belong to the same chemical family, the similarity of molecular structure is most completely and most easily produced, and such crystals are *isomorphous*. Examples.—Sulphate of zinc and sulphate of magnesia, carbonate of lime and carbonate of zinc, sulphate of barytes and sulphate of strontia.

3d. But identity of molecular structure may result from the aggregation of substances the most different in their chemical relations, and hence isomorphous bodies are not necessarily of similar chemical constitutions.

4th. As the influence of the chemical constitution does not extend to the absolute determination of the molecular structure, a body, chemically the same, may assume incompatible crystalline forms, and so become *dimorphous;* but as the chemical structure influences the molecular arrangement in some degree, dimorphous bodies, which are isomorphous in one form, are generally so in the other, they are *isodimorphous*. Examples.—Sulphur, bisulphate of potash, nitrate of potash and carbonate of lime, garnet and idocrase, arsenious acid and oxide of antimony.

5th. We cannot assert that the similarity of form of truly isomorph-

ous bodies results from the isomorphism of their elements; for, so far as our observation goes, their simple constituents are not necessarily, or even usually isomorphous. Examples.—Arseniates and phosphates, sulphates and seleniates.

6th. We cannot assert that isomorphism results from the aggregation of the same number of simple molecules; for we do not know what bodies are truly simple, nor do we know, without doubt, that we can value the relative number of atoms present; but, even in the existing state of our knowledge, we have numerous examples of bodies truly isomorphous which contain an unlike number of atoms according to our present ideas. Examples.—Potash and ammonia, natrolite and mesotype, sulphur, feldspar, and bisulphate of potash.

Finally. Isomorphism does result from the aggregation, according to the same laws, of similar molecular groups, which are most generally formed by the reunion of similar chemical substances in the same state of combination.

SECTION III.

OF DIMORPHISM AND ISOMERISM, AND OF THE THEORY OF TYPES.

The fact of the same body being capable of crystallizing in forms belonging to two different systems has been already frequently referred to, but, for convenience of reference, a more detailed list of such cases is here inserted, taken from Professor Johnston's excellent report on the subject made to the British Association.

	Symbol or Form.	Crystalline Form.
I. *Elementary bodies:*		
Sulphur . . . . . A	S.	Rt. Rh. Pr., M. on M. 101·59, *Haid.*
——— . . . . . B		Oblique Rh. Pr. of 90° 32′, *M.*
Carbon . . . . . A	C.	Reg. Octohedron.
——— . . . . . B		Rhombohedral.
II. *Bi-elementary Compounds:*		
Dioxide of Copper . A	Cu_2O.	Cube.
——— . B		Rh. of 99° 15′, 6 sid. Pr. Rhomb. cleav., *Sk.*
Disulphur. of Copper A	Cu.S. or Cu_2S.	Do., Primary a Rhomb., P. on P′. =71° 30′.
——— B		Reg. Octohedrons.
Sulphuret of Silver . A	Ag.S. or Ag_2S.	Cube in Silver glance.
——— . B		Rhomboid.
Sulph. of Manganese A	Mn.S.	Cubes.
——— B		Rhomboid.
Bisulphuret of Iron . A	$Fe.S_2$.	Cubes.
——— . B		Rt. Rh R., M. on M′. 106° 2′.
Biniodide of Mercury A	$Hg.I_2$.	Octohed. with square base.
——— B		Rt. Rh. Pr., M.M.=114°.
Bichlor. of Mercury . A	$Hg.Cl_2$.	Rt. Rh. Pr., M.M.=71·55.
——— . B		Octohed. with rect. base.
Arsenious acid . . A	As_2O_3.	Reg. Octohedrons.
——— . . B		Rt. Rh. Pr.
Oxide of Antimony . A	Sb_2O_3.	Do., M. on M′. 136° 58′.
——— . B		Reg. Octohedrons.
III. *Compounds of* 3 *Elements:*		
Carbonate of Lime . A	$Ca.O.+C.O_2$.	Rhomb. of 105° 4′, *M.*
——— . B		Rt. Rh. Pr. of 116° 16′, *Ku.*
Carbon. of Magnesia A	$Mg.O.+C.O_2$.	Rhomb. of 106° 15′.
——— B		Rt. Rh. Pr.
Carbonate of Iron . A	$Fe.O.+C.O_2$.	Rhomb. of 107·0.
——— . B		Rt. Rh. Pr., 108° 26′, 118° 0′?
Carbonate of Lead . A	$Pb.O.+C.O_2$.	Rhomboid, 104° 53½′?
——— . B		Rt. Rh. Pr. of 117° 14′, *Ku.*
Nitrate of Potash . A	$K.O.+N.O_5$.	Rt. Rh. Pr., M. on M′.=118° 52′, *Lv.*
——— . B		Rhomboid of 106·36, *Fm.*
Chromate of Lead . A	$Pb.O.+Cr.O_3$.	Ob. Rh. Pr.
——— . B		Square Prism.
IV. *Compounds of* 4 *or more Elements:*		
Sulphate of Nickel . A	$Ni.O.+S.O_3+7H.O$.	Rt. Rh. Pr., M. on M′. 91° 10′, *Bk.*
——— . B		Square Prism.
Seleniate of Zinc . A	$Zn.O.+Se.O_3+7H.O$.	Rt. Rh. Pr.
——— . B		Square Prism.
Bisulphate of Potash A	$\overline{K.O.+S.O_3}+\overline{H.O.+S.O_3}$.	Rhombic Octohed. (form of sulphur), *M.*
——— B		Ob. Rh. Pr. (form of feldspar), *M.*
Biphosphate of Soda A	$\overline{Na.O.+P_2O_5+4H.O.}$	Rt. Rh. Pr. of M. on M′. 93° 54′.
——— B	or. $\dot{\mathrm{Na}}.\dot{\mathrm{H}}_2\ddot{\dot{\mathrm{P}}}.+2\dot{\mathrm{H}}$.	Do. of 78° 30′.
Garnet . . . . . A	$\dot{\mathrm{Ca}}_3\dddot{\mathrm{Si}}.+\left.\frac{\dddot{\mathrm{Al}}.}{\dddot{\mathrm{Fe}}.}\right\}\dddot{\mathrm{Si}}.$	Reg. Dodecahedron.
Idocrase . . . . . B		Square prism.
Baryto-Calcite . A	$\left.\begin{matrix}Ca.O.\\Sr.O.\end{matrix}\right\}C.O_2+\left.\begin{matrix}Ba.O.\\Sr.O.\end{matrix}\right\}C.O_2$.	Oblique Rh. Prism.
——— . . B		Right Rh. Prism (form of arragonite).
Sulphato-Tricarbonate of Lead . .	$\dot{\mathrm{Pb}}.\dddot{\mathrm{S}}.+3\dot{\mathrm{Pb}}.\ddot{\mathrm{C}}.$	Acute rhomboid of 72° 30′.
		Rt. Rhomb. Prism,* M. on .M=120.

* Haidinger says an oblique rhombic prism, which, according to the subsequent measurement of Brooke, is in correct. *Bk.*, Brooke *Ku.*, Kupfer; *Lv.*, Levy; *M.*, Mitscherlich; *Sk.*, Suckow.

The molecular arrangements which produce this diversity of form are not in general of equal stability; on the contrary, one figure appears to be in general forced upon the body, and is abandoned by it upon very slight disturbance. Thus, when a prism of arragonite is heated in the flame of a spirit-lamp, it breaks up into a congeries of little rhombs of common calc spar at a temperature far below that at which the carbonate of lime commences to be decomposed; but no alteration of temperature can convert calc spar back again into arragonite. Indeed, arragonite appears to be formed only between very narrow limits of temperature. When chalk is melted, it forms, on cooling, marble, whose fracture shows it to have the rhombohedral structure; and when carbonate of lime is precipitated at ordinary temperatures, the microscopic crystals produced are rhombohedrons; but when it is precipitated from a boiling solution, it deposites minute crystals of arragonite, which a hi her or a lower temperature would have prevented.

When sulphur has been crystallized by fusion in oblique rhombic prisms, these lose their transparency after a day or two, and change into a mass of very minute right rhombic octohedrons. When the arsenious acid is crystallized in rhombic prisms, it alters slowly, and eventually becomes a dull white mass, which is a congeries of regular octohedrons; but if the rhombic form of the acid be dissolved in muriatic acid, and the solution set to crystallize, it is deposited in the octohedral form, and the formation of each crystal is accompanied by a brilliant flash of light, indicating probably the moment of the change of molecular condition. One form is therefore the stable condition of arrangement, the other being produced by the sudden fixation of the molecules in a form which is naturally only transitive, and from which they free themselves as soon as the external circumstances admit of their suitable motion among each other.

Independent of the change in external figure, dimorphous bodies present remarkable differences in physical properties; thus the density is generally different; in one form the substance is more soluble than in the other; they differ also in hardness, and, generally speaking, in all characters derived from the physical arrangement of molecules.

A body in its dimorphous conditions presents frequently a difference of chemical properties deserving of particular notice. The bisulphuret of iron, in its cubical form, is remarkably permanent, not being acted on either by air or water; but in its right rhombic form, when exposed to moist air, it absorbs oxygen with avidity, and is converted into a crystalline mass of copperas. On this principle depends, most probably, the change of molecular condition which takes place in oxide of chrome, peroxide of tin, zirconia, and alumina, when exposed to a temperature just below redness. These substances, which had been easily soluble in acids, become almost totally insoluble, except in boiling oil of vitriol, and this change is generally accompanied by the spontaneous ignition of the body, which the temperature applied would be quite insufficient to produce.

Independent of crystalline form, we must refer to circumstances

similar to those which produce dimorphism, a variety of differences in physical constitution observable in certain bodies; thus melted sulphur is, at 230° F., perfectly liquid; on being heated to 430° it becomes thick, and so tenacious that the vessel containing it may be inverted without it running out; when heated farther to 480°, it becomes again liquid, and continues so till it begins to boil. When the red oxide of mercury is heated nearly to redness, it becomes almost quite black. If the red iodide of mercury, formed by precipitation, be sublimed, it becomes yellow; but if the sublimed mass be scratched with a pin, the edges of the scratch turn red, and the redness spreads from thence until the whole mass is converted into its original condition. Even in liquids and gases, this difference in molecular condition, whether produced by temperature or by other causes, appears frequently to occur. Thus the liquid hyponitrous acid ($N.O_3$) is deep green at 60°, but at 4° it is quite colourless; and the deep red gas of nitrous acid ($N.O_4$) becomes, when heated to 212°, absolutely black and opaque. The compound of starch and iodine, so beautifully blue-coloured at ordinary temperatures, becomes colourless when heated to 200°, but acquires its original tint in proportion as it again cools. In all such cases, there is scarcely room to doubt but that, if we had as perfect methods of determining the molecular structure as is afforded by the measure of the angles and the optical properties of the bodies when crystallized, we should find these phenomena to depend upon causes of the same kind.

In solid bodies, a difference of molecular structure, fully equivalent to that to which dimorphism may be referred, is capable of being produced by very simple means. Thus, when a plate of glass is compressed by means of a screw, it assumes a doubly refracting structure, and gives with polarized light a cross and rings, variously disposed according to the direction of the pressure. In this case, the change of structure arises necessarily from an increase of density in the compressed portions; but the same effect may be produced by the converse process; a plate of glass which has been suddenly cooled from having been red-hot, assumes a similar doubly refracting and polarizing structure, although here the density is diminished in place of being increased. I have found the sp. gr. of glass suddenly chilled to be about $\frac{1}{100}$ less than that of glass of the same kind which had cooled slowly, indicating that the volume was the same that it had occupied at a dull red heat, and that hence the internal molecules were arranged so as to occupy a greater space than in the usual condition.

The differences of chemical properties may, however, proceed much farther, so that in place of considering that there is one chemical substance which may exist in two molecular conditions, we are obliged to consider that the individuality of the body is lost, and that in its two forms it constitutes two distinct and independent chemical substances. Thus, by the action of sulphuric acid on alcohol, we obtain a gas consisting of carbon and hydrogen, in the proportion of an equivalent of each. In the destructive distillation of wood, a solid substance is obtained, fusible like wax, and volatile only at a high temperature; this consists also of carbon and hydrogen, and in the same proportions. These elements, so combined, present,

therefore, a difference in molecular arrangement still greater than those which have been observed among merely dimorphous bodies, and when we examine their chemical relations, the diversity becomes still more marked. The gas (olefiant gas) is remarkable for the number of compounds to which it gives rise, and has been, from the variety of its reactions, of great influence on the existing theories of organic chemistry. The solid is inattackable even by the strongest agents, and, from its total indifference to combination, has been called paraffine (parum affinis.) In this case, the difference of properties indicates a difference of structure much more profound than that by which change of density, colour, or even crystalline arrangement could have its source; it is not merely that the molecules are differently placed, but that the molecules are different; the carbon and hydrogen which unite to constitute the chemical equivalent of the body are themselves differently arranged, and thus give rise to difference of properties; and the physical molecules formed by their reunion being again grouped according to dissimilar laws, produce the diversity of physical properties and states of aggregation; the bodies being thus in every property unlike, are to be looked upon as independent substances; they are said to be isomeric (from ισος μερος) because they have the same ultimate composition, but in all their chemical relations they may differ as widely as bodies which have no element in common.

When, therefore, the groups of chemical molecules are differently arranged, the various differences in colour, density, solubility, and figure which belong to dimorphous bodies are produced; but when the difference of arrangement extends to the chemical constituents of these molecular groups, independent, but isomeric bodies are produced.

It is generally found that this difference in the constitution of the chemical molecule has the effect of changing, in a simple manner, the equivalent number of the body. Thus oil of turpentine and oil of citron are isomeric, each having the composition C_5H_4; but when we combine these oils with muriatic acid, we find that the equivalent group of oil of turpentine contains $C_{20}H_{16}$, while that of oil of citron is only $C_{10}H_8$; it is remarkable that, though the chemical group of oil of citron is only one half the weight of that of oil of turpentine, it exercises the same power of circular polarization, but in the opposite direction. Another example of this simplicity of proportion in weight between the equivalents of isomeric bodies, is met with in common alcohol and methylic ether, that of the former being $C_4H_6O_2$, that of the latter being C_2H_3O.

The difference of the chemical constitution in isomeric bodies is not limited to magnitude, as determined by the weight of their equivalent, but extends to internal structure. Thus alcohol is composed of ether and water, $C_4H_5O.+H.O.$, while methylic ether cannot be resolved into those substances. Formiate of methylene and glacial acetic acid are each $C_4H_4O_4$, not differing even in the weight of their equivalent; but all the properties of these bodies show that glacial acetic acid is $C_4H_3O_3+H.O.$, while formiate of methylene is $C_2H.O_3+C_2H_3O$. Instances of this kind might be multiplied to any extent, but these will be sufficient to illustrate the principle.

It is necessary, however, in studying such cases of isomerism, to bear in mind what has been so beautifully shown by Graham, that the presence of foreign bodies, in quantities so small as to be totally unappreciable, except in the most rigidly accurate analysis, may change so completely the properties of bodies that they will simulate isomerism. Thus phosphuretted hydrogen may exist in two conditions, in one of which it is spontaneously inflammable, and in the other not. They both give, on analysis, the same formula, $P.H_3$; but the first may be changed into the second by mere admixture with a very small quantity of the vapour of ether, and the second may be converted into the first by the most minute bubble of nitrous acid gas. Such bodies, therefore, which owe their diversity of properties to accidental circumstances, are not isomeric, and must be carefully distinguished from those before described.

As we have thus traced a gradual transition from the feeblest indications of dimorphism, to the complete difference of structure and properties constituting isomerism, it becomes an interesting question whether we may not have occasion to retrace our steps, and to seek in those bodies which we have hitherto considered as only differing in physical properties, for evidence of difference in chemical arrangement. May not a simple substance, as sulphur or antimony, enter into combination with equivalents of different weights, and so resemble oil of turpentine and oil of citron; and may not this difference in equivalents be the source of diversity in form? When sulphur crystallizes in the form of bisulphate of potash, may we not reasonably suppose that its molecules are grouped into a complex figure, like that of the compound salt, and that its equivalent is, in proportion, greater than when it crystallizes as a simple body? We say that two ordinary equivalents of manganese replace one of chlorine, but is it not really that when manganese replaces chlorine, its equivalent is double what it is when it replaces hydrogen or copper? Manganese replacing chlorine, is to manganese replacing copper, what oil of turpentine is to oil of citron; and hence it may be isomeric with itself, for the functions it performs in its two modes of combination are the most widely different possible. The bisulphuret of iron, in its cubical form, is $Fe.S_2$, and, like $Mn.O_2$, is decomposed only by a red heat, when it parts with one third of its volatile constituent; but in its rhombic form, may not its equivalent be Fe_2S_4, resembling $Cl.O_4$, and, like it, be decomposed by the slightest causes?

The circumstance that isomeric bodies are almost universally connected by simple relations between their atomic weights, coupled with the idea that even among the simple bodies a kind of isomerism may be the cause of their dimorphous conditions, acquires remarkable interest from the fact that the equivalent numbers of many of the simple bodies are closely related to one another, as is shown in the following table:

1½	equivalent of	bismuth	= 106·65	1	equivalent of	zinc	= 32·31
2	"	palladium . . .	106·72	1	"	yttrium . . .	32·25
2	equivalent of	osmium . . .	199·72	¼	"	antimony . . .	32·40
1	"	gold	199·21	½	"	tellurium . . .	32·13
				2	"	sulphur . . .	32·24
1	equivalent of	platina	98·84				
1	"	iridium . . .	98·84	1	equivalent of	cobalt	29·57
1	equivalent of	molybdenum . .	47·96	1	"	nickel	29·62
½	"	tungsten . . .	47·40	½	"	tin	29·46

May it not be possible that science shall hereafter find the metals so connected to be truly isomeric? In no case are their properties more different; and we find in the racemic and tartaric acids an example of the general similarity of properties in the compounds of isomeric bodies, which is so remarkable in the combinations of sulphur and tellurium, or of cobalt and nickel, among the simple substances.

Considerable probability is given to the idea of the compound nature of bodies at present considered simple, by the existence of certain compound bodies which simulate the properties of, and enter into combination subject to the same laws as the undecompounded substances. Thus carbon and hydrogen unite to form a gas, cyanogen, which combines with the metals, with oxygen, with hydrogen, &c., precisely as chlorine does; it is the origin or root of a series of cyanides, as chlorine is of a series of chlorides, and it is hence called a compound radical. The discovery of this principle by Gay Lussac was the foundation of all that is exact and philosophical in our views of organic chemistry. Bodies which contain the same ultimate elements may be different, because they contain different radicals, precisely as the salts of nickel and the salts of cobalt will remain quite distinct, even should nickel and cobalt be hereafter shown to be isomeric bodies. This principle of compound radicals is so beautiful and so easily applied, that its use has been, as I conceive, somewhat too extensively adopted; and hence, wherever simplicity of expression was sought for, or a difference of properties was to be explained, the formulæ of organic bodies were perhaps too hastily grouped, by the assumption of a hypothetic radical, of which the different bodies of the series were supposed to be combinations. It is certain that, in many cases, this plan has been of great use to science, as in the benzyle theory of Liebig, and in the ether and ammonia theories proposed by Berzelius and myself; but I consider the degree to which it has latterly been extended, by which the existence of a great variety of bodies has been assumed, for which there is scarcely any reason, except some additional simplicity of formulæ, which often served to conceal the truth, to have been productive of much disadvantage to true science and a misdirection of thought, which we should seek as much as possible to avoid.

In all that has been described of the arrangement of the elements of compound bodies, their union has been considered as resulting from their antagonistic and mutually neutralizing properties, and the successive stages of composition being effected in binary groups: thus crystallized alum is a compound of water and dry alum; this last, a compound of sulphate of potash and sulphate of

alumina; these respectively, compounds of sulphuric acid and a base which consists of oxygen united to a metal; the sulphuric acid it self being formed by the union of oxygen and sulphur. This view results necessarily from what has been said of the nature of chemical affinity, and expresses faithfully the principle upon which the electro-chemical theory has been formed; there is no doubt but that the constitution of inorganic bodies is regulated in this way, but we meet with considerable difficulty in applying its principles to organic chemistry. Thus I myself suggested a few years ago, that the formic and acetic acids should be looked upon as oxides of compound radicals, formyle and acetyle, $C_2H.O_3=Fo.O_3$ and $C_4H_3O_3=Ac.O_3$, by which means a variety of bodies of analogous constitution were simply connected together, as the formyle or acetyle, which combine with oxygen to form those vegetable acids, combine with iodine, chlorine, sulphur, and cyanogen to form binary compounds, precisely as manganese (a simple radical) combines with oxygen to form manganic acid, and with chlorine, &c., to form an analogous series of bodies. I am far from abandoning this view: the question of its full applicability will be discussed among the general laws of organic chemistry, but at present we will attend to only one circumstance connected with it. Hydrated acetic acid is formed from alcohol, by the latter losing two equivalents of hydrogen, and gaining two of oxygen in their place; and in like manner, hydrated formic acid is produced from pyroxylic spirit, by losing H_2 and gaining O_2, thus:

Alcohol	$C_4H_6O_2$	Pyroxylic spirit . .	$C_2H_4O_2$
gives by . .	$-H_2+O_2$	gives by . .	$-H_2+O_2$
Hydrated acetic acid .	$C_4H_4O_4$.	Hydrated acetic acid .	$C_2H_2O_4$.

Now, if acetic acid contains acetyle, does it exist in alcohol; or must we consider that, by the gradual process of oxidation, the molecular structure of the alcohol is totally broken up, and that the acetic acid formed has no natural or necessary connexion with it?

We owe to Dumas the introduction of a principle into organic chemistry, which, applied to changes such as those described above, promises to shed considerable light upon the reactions and constitution of organic bodies; but it yet involves conditions so opposed to our present ideas of chemical affinity, that we can only look on it as a proposition which merits profound attention. He considers that the elements of organic bodies are not united by affinity arising from opposition of properties, but that they represent a group of molecules connected by a single force, precisely as the planetary masses are by gravitation, and just as any of the planets might be replaced in the solar system by a ball of matter of totally different chemical properties, provided its gravitating mass remained the same, without disturbing in the least the conditions of mechanical equilibrium; so, in an organic substance, elements of the most diverse characters may be substituted for each other, and yet the molecular group remain unaltered in structure and physical constitution. Thus the molecular group of alcohol ($C_4H_6O_2$) contains twelve chemical atoms. When it is changed into acetic acid ($C_4H_4O_4$), the number of chemical atoms is the same; the mechanical type of

the body is unaltered, although its chemical properties are completely changed and a new substance formed. Bodies, therefore, are classified by Dumas according to certain types or models. When the number of molecules in the equivalents of the bodies remains the same while the nature of the elements changes, the bodies have the same mechanical type; but if the substitution of elements is accompanied by a change of properties, the chemical type of the original body is destroyed. Thus alcohol and acetic acid have not the same chemical type.

When acetic acid is treated with chlorine, it loses three equivalents of hydrogen and gains three of chlorine ($C_4H_4O_4—H_3+Cl_3= C_4Cl_3H.O_4$), forming chloroacetic acid. The sum of the molecules is here twelve, and this substance has the same mechanical type as alcohol and common acetic acid; but in changing to this body, common acetic acid scarcely changes its properties, and hence is said to retain its chemical type. When ether ($C_4H_5O.$) is treated with chlorine, its hydrogen is totally replaced by chlorine, and the body ($C_4Cl_5O.$), chlorine ether, is produced; the number of molecules being the same, the mechanical type is preserved; but more, the chlorine ether combines with acids forming salts like those of common ether, which it resembles in all essential chemical characters, and hence, in this case, the chemical type is undisturbed, notwithstanding the total substitution of chlorine for hydrogen, a body differing from it so much in general characters.

The question how far this theory of types should be adopted, and how far the law of substitution on which it rests is verified by experiment, will be hereafter examined. The theory is here only noticed as involving important relations between the mechanical structure and the chemical constitution of organic bodies.

SECTION IV.

OF CATALYSIS.

The decomposition of compound bodies is frequently effected by the intervention of causes which cannot be referred to ordinary affinity; and in many cases, bodies which have but little tendency to unite, enter into combination when brought into contact with a substance for which neither has affinity, and which remains, after the action is completed, perfectly unaltered. Thus, when hydrogen and oxygen, mixed together in a gaseous form, are brought into contact with a clean slip of platinum, they gradually unite, and so much heat may be evolved by their rapid combination as to ignite the platinum, and explode the remainder of the gas. In this case we seek to explain the phenomenon by supposing that the platinum condenses powerfully on its surface a layer of mixed gaseous particles, and thus brings them within the sphere of their mutual attraction. But this explanation does not apply to other cases. If we boil starch ($C_{12}H_{10}O_{10}$) with diluted sulphuric acid, it is converted successively into dextrine, gum, starch-sugar, and, finally, crystallizable grape-sugar ($C_{12}H_{12}O_{12}$), having associated to itself the constituents of two equivalents of water. At the termination of the process, the sulphuric acid is found unaltered in properties and in quantity, so

that the smallest portion of sulphuric acid is sufficient to convert into sugar an indefinitely great quantity of starch. If oxamide ($C_2O_2N.H_2$) be diffused through water, in contact with the smallest possible quantity of oxalic acid, it gradually disappears, and, appropriating to itself the elements of an equivalent of water, is converted into neutral oxalate of ammonia, ($C_2O_3+N.H_3$), the small quantity of oxalic acid originally added remaining unaltered and in excess.

Among instances of decomposition by forces of this kind, the oxygenated water ($H.O_2$) may be taken as an example. This substance, when pure, separates spontaneously, after some time, into water and oxygen gas, but its decomposition may be rendered violent and instantaneous by putting it into contact with finely-divided metallic platinum, or metallic silver, or black oxide of manganese, or fibrine, or a variety of other bodies. In all these cases, the body added remains quite unaltered; no affinity can be traced between it and the oxygenated water, the mere presence of the foreign body appearing to cause the decomposition.

Berzelius, who first directed general attention to these phenomena, proposed to attribute them to a peculiar force, differing from ordinary affinity. When one body is decomposed by another, in virtue of a superior affinitary power, the decomposing body combines with one element of the body which is decomposed, and the other is then expelled. It is in this way that we obtain the constituents of bodies by ordinary *analysis;* and for distinction, he proposes to term such decompositions as those just described, operations of *catalysis*, and to name the power which these bodies have of acting by mere contact, a *catalytic force.*

It is evident, certainly, that by giving a name to this class of phenomena, we are enabled usefully to contemplate them as a group, and to examine more easily their relations to each other and to ordinary action; yet the word *catalysis* really teaches us nothing of the phenomena, and it is, indeed, improbable that such varied cases of union and separation should be derivable from one single force. It is hence necessary, before concluding on the nature of this action, to trace it through a greater variety of cases, and to revert briefly to the conditions of affinity by which the elements of compound bodies are held together.

The elements of a compound substance are retained together in a certain molecular arrangement, because the affinities are then satisfied; but it is natural to suppose that, while the elements remain the same, their affinities for each other might be just as completely satisfied by a different molecular arrangement. The original body might therefore be changed into another, by a change in the action of its own particles, independent of any substance acting chemically on it from without; and hence the principle of catalytic decomposition resolves itself into a means of disturbing the molecular equilibrium of a compound body, so that it can be only restored when the particles are differently arranged. Catalysis may, therefore, be produced not merely by the presence of various bodies, but still more remarkably by the action of physical agents, among which heat is the most powerful; thus, when acetate of lime ($C_4H_3O_4Ca.$) is strongly heated, the equilibrium of its molecular group is over

turned, and when the affinities again satisfy themselves, two new bodies result, acetone and carbonate of lime (C_3H_3O. and $C.O_3Ca$.). Destructive distillation is therefore a catalytic process, and the origin of all pyrogenic products is to be traced to the new conditions under which the affinities are satisfied, which had originally united the elements of the body exposed to heat. The sudden decomposition of explosive bodies by an elevation of temperature or by a slight blow, is traceable to the same disturbance of the old equilibrium, and establishment of the new. A most important means of thus setting into motion the particles of bodies, and enabling them to rearrange themselves under new forms, consists in bringing them into contact with a substance already in a state of decomposition; thus, if oxygenated water be brought into contact with oxide of silver, the decomposition is propagated to the latter, which is completely resolved into oxygen and metallic silver; if peroxide of lead be used, it is converted into protoxide by the escape of half its oxygen, and even the black oxide of manganese may be reduced to the state of protoxide if the solution contain an acid; in all these cases, the decomposition, which commenced with the oxygenated water, extends to the metallic oxide, in virtue of the motion communicated to their particles, enabling the new arrangement to be effected. In some instances, in organic chemistry, this principle is still more beautifully shown. If a solution of sugar ($C_{12}H_{11}O_{11}$) be brought into contact with a little decomposing gluten or yeast, it unites with the elements of an equivalent of water, and divides itself into two equivalents of alcohol, 2 ($C_4H_6O_2$), and four of carbonic acid, 4 ($C.O_2$). If a solution of urea ($C.O.N.H_2$) be put in contact with yeast, it unites also with an atom of water, and is then decomposed into an equivalent of ammonia ($N.H_3$) and one of carbonic acid. The conversion of starch into sugar in the processes of germination and of malting, is effected by a substance which accompanies the starch in the grain. This substance is called diastase, and is analogous in most of its properties to vegetable gluten. The slow decomposition of the diastase communicates to the molecules of many thousand times its weight of starch the degree of motion necessary for their rearrangement, and the appropriation of the elements of water requisite for the formation of starch-sugar.

If platinum, which is, by itself, totally unacted on by nitric acid, be alloyed with silver, the alloy dissolves in dilute nitric acid without leaving any residue. Pure copper is not acted upon by dilute sulphuric acid; but when it is alloyed with nickel and zinc, as in the argentine, or German silver of commerce, it dissolves completely. In these cases, the molecular action which produces the combination with the acid was not possessed by the platina or copper when alone, but is acquired by them, being transmitted from the other metals with which they are alloyed.

It may not be easy to reduce to the action of this principle all phenomena of catalysis; for, in the imperfect light by which we contemplate them, it is possible that we may rank together circumstances whose real nature is very different; but, at all events, we must recognise in this principle, the definite introduction of which into science is due to Liebig, a cause of chemical decomposition

peculiarly important in explaining the complex reactions of organic bodies. It is remarkable, also, that this law, of which the simplest expression is, that where two chemical substances are in contact, any motion occurring among the particles of the one may be communicated to the particles of the other, is of a more purely mechanical nature than any other principle as yet received in chemistry; and when more definitely established by succeeding research, it may be the basis of a dynamical theory in chemistry, as the law of equivalents and of multiple combination expresses the statical condition of bodies which unite by chemical force.

We must, at least, look upon these actions of catalysis, the con ditions of molecular arrangement which give rise to isomerism and dimorphism, and the introduction of the principle of types in oppo sition to that of mere binary combination, as tending towards a change in our ideas of the nature of chemical affinity, which may, before long, remodel the whole constitution of the science.

CHAPTER XI.

ON THE CLASSIFICATION OF THE ELEMENTARY BODIES.

THE principal classifications of the simple bodies that have been proposed are those of Berzelius, founded on their electro-chemical relations, and of Thompson, who divided them into supporters and non-supporters of combustion. It has, however, been fully shown, that in combustion each body is mutually a supporter and a combustible: oxygen burns in hydrogen or in the vapour of sulphur, just as much as hydrogen or sulphur burn in oxygen; Thompson's principle is therefore radically defective; and the electro-chemical theory, although far superior as a principle, is liable to weighty objections of a somewhat similar kind. These have been already, however, so far noticed, and the arrangement of the simple bodies in that series so fully given, p. 188, that it is unnecessary to recur farther to the subject.

The kind of classification that is suited to the present wants of chemistry must be founded upon the general analogy of properties between substances belonging to the same class, and on their isomorphous replacement of one another. This last character is not absolute; for, from the dimorphism of many of the simple bodies, it is often difficult to assign their true crystalline relations to each other, and in many cases we do not possess any positive information of their forms.

Graham has recently proposed a classification which expresses, more completely than any other, the natural relations of the simple bodies. The first class consists of oxygen, sulphur, selenium, and tellurium. The parallelism in properties of the last three is complete, and their compounds are strictly isomorphous; their similarity to oxygen is not so perfect, but they resemble it in their method of combination and in the characters of the substances which they form in uniting with hydrogen and the metals.

The second class comprises magnesium, calcium, manganese, iron, cobalt, nickel, zinc, cadmium, copper, hydrogen, bismuth, chromium, aluminum, glucinum, vanadium, zirconium, yttrium, thorium. The similar salts of the protoxides of this class are isomorphous; and, as has been already shown under the head of Isomorphism, two equivalents of a protoxide of this class replace one equivalent of an alkali. Chromium, aluminum, glucinum, vanadium, and zirconium do not form protoxides, but sesquioxides, the salts of which are isomorphous with those of the sesquioxides of iron and manganese. A remarkable connexion is established between this class and the preceding by the ismorphism of the manganic acid ($Mn.O_3$) and chromic acid ($Cr.O_3$) with sulphuric acid ($S.O_3$), indicating that under certain circumstances these metals may change from one natural family to another.

The third class contains barium, strontium, and lead. Their salts are strictly isomorphous, and they are connected together by great similarity of chemical properties. Thus the sulphates of the metals of the second class are soluble in water, while the sulphates of this class are almost insoluble. Calcium approximates to this condition by the sparing solubility of sulphate of lime; and the connexion between the two families is still more fully shown by the dimorphism of carbonate of lime, it having in one form the figure of the carbonates of magnesia and of iron, and in the other that of the carbonates of barytes and of lead.

The fourth class consists of potassium, sodium, and silver. The similarity of chemical properties of potassium and sodium is sufficiently evident; and although their compounds are not frequently isomorphous, yet there is good reason for attributing that to the dimorphism of each. Silver differs remarkably in its chemical relations from potassium and sodium, and the only grounds for inserting it in this class is the isomorphism of sulphate of silver with anhydrous sulphate of soda.

The salts of potash are perfectly isomorphous with the salts of ammonia which contain an atom of water; and hence, if the base of the ammoniacal salts ($N.H_3+H.O.$) be written $N.H_4 . O.$, it may be considered as an oxide of a compound radical which is isomorphous with potassium, and would rank, did we not know its composition, in the present group. This view of the composition of the ammoniacal salts was suggested by Berzelius, who gave to that compound radical the name ammonium; but I have since shown that the replacement is really by two equivalents of a hydrogen compound, as already noticed in speaking of the second class.

Fifth class, chlorine, iodine, bromine, and fluorine. This group is best characterized by similarity of chemical properties; and, so far as observation extends, their isomorphism appears to be complete. It is connected with the first and second classes by means of manganese, of which two equivalents replace, in truly isomorphous compounds, one of chlorine.

Sixth class, nitrogen, phosphorus, arsenic, and antimony. In their chemical history these compounds exhibit considerable, though not complete similarity. The corresponding compounds of arsenic, antimony, and phosphorus are generally isomorphous, but in no case

has isomorphism been observed between their compounds and those of nitrogen. A certain analogy appears to exist between nitrogen and the substances of the fifth class, as the nitric acid corresponds remarkably in properties to the chloric and iodic acids, with which, however, it is not isomorphous. Nitrogen appears also to replace oxygen in many cases in the proportion of one third of its equivalent weight.

Seventh class, tin and titanium, connected by the isomorphism of titanic acid and peroxide of tin.

Eighth class, silver and gold, from their isomorphism in the metallic state.

Ninth class, platinum, palladium, iridium, and osmium, from the isomorphism of their double chlorides, by which also Graham considers this class to be connected with the seventh.

Tenth class, tungsten and molybdenum; the tungstates and molybdates being isomorphous. These metals will probably be found to be of the same family with chrome, as chromate of lead has been found crystallized in the same form as the molybdate.

Eleventh class, carbon, boron, and silicon: of these substances no isomorphous relations are known; they are brought together by a general, though imperfect analogy of properties.

Graham makes no attempt at classifying mercury, cerium, columbium, lithium, rhodium, or uranium.

I agree completely with the general principles of this classification, but, in a few cases, researches made since it was drawn up by Graham render some alterations necessary; thus the similarity of constitution between the compounds of bismuth and copper, which had induced him to insert bismuth in the second class, has no real existence, and I would transfer it to the same class with antimony; their sulphurets being isomorphous, and their chemical properties being, generally speaking, very similar. Indeed, it is almost certain that the oxide of bismuth is not a protoxide, but a sesquioxide, and hence corresponds to the oxide of antimony.

I do not consider the isomorphism of sulphate of soda and sulphate of silver as being a sufficient ground for ranking the latter metal in the fourth class. We have already seen numerous examples of isomorphism among substances of totally different chemical constitution, and the properties of the compounds of silver resemble so completely those of lead, as to demonstrate positively that it belongs to the same natural group. When copper enters into combination in a double equivalent Cu_2, it becomes likewise a member of the lead and barytes group, as is shown by the sparing solubility of its sulphate and chloride; and its being isomorphous with silver furnishes additional evidence of its true position.

Silver and gold being isomorphous only in the regular system, and their compounds being totally dissimilar in constitution, I do not retain the eighth class of Graham.

I have satisfied myself of the perfect analogy of palladium with copper; it therefore must be separated from platinum, and removed to the second class. When mercury enters into combination with the equivalent 101,4 (Hg.), it coincides in the nature of its compounds with palladium and copper, and attaches itself to the second

class; but when its equivalent is 202,8 (Hg_2), its compounds resemble those of lead and silver, and, like copper, it then becomes a member of the third class.

A classification such as this, although necessary for the philosophical study of the relations of the simple bodies, could not, without considerable inconvenience, be strictly adhered to in an elementary work like this; I shall, therefore, having thus laid down these general principles, place it for a time aside, and commence the study of the non-metallic bodies, and their compounds with each other, without reference to any arrangement, except that of treating first those subjects that may be useful towards understanding or illustrating those that follow.

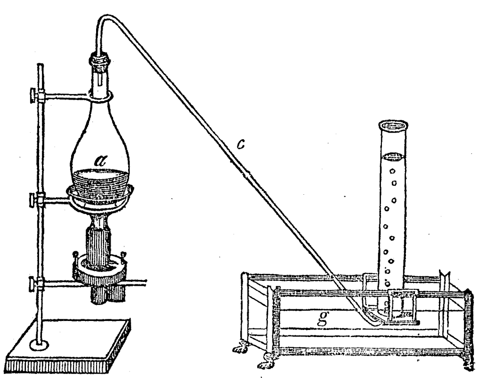
CHAPTER XII.

OF THE SIMPLE NON-METALLIC BODIES, AND THEIR COMPOUNDS WITH EACH OTHER.

Of Oxygen.

From the great quantity in which it exists in nature, the numerous processes into which it enters as an agent, and the influence which its discovery exercised upon the progress of chemical theory, oxygen may be looked upon as the most important of the simple bodies. It constitutes more than a fifth of the atmosphere by which our planet is invested, eight ninths of the whole quantity of water which exists upon its surface, and, besides existing in great quantity in most animal and vegetable bodies, it forms at least a third of the total weight of the mineral crust of the globe. On it the processes of combustion and of respiration are dependant, and the functions of organized existence, in both its forms, are essentially connected and sustained through its agency.

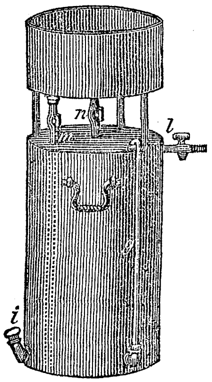
Oxygen exists only under the form of gas; it is colourless and transparent; its specific gravity is 1102·6; 100 cubic inches of it weigh 34·2 grains; its refractive index is 0·8616, that of air being 1·0000. It is very sparingly dissolved by water, 100 cubic inches of water taking up only between three and four of the gas. It is, consequently, in most cases, collected over water, by forms of apparatus that shall be now described.



H H

For the collection and preservation of gases, such as oxygen, the instruments generally employed are the pneumatic trough and the gasometer. The former is any ves-

sel, *g*, containing water, for such gases as are not absorbed by it, in which is inverted a glass vessel full of water, which is sustained in it by the pressure of the external air, as is the mercury in the tube of the barometer. The orifice of the tube *c*, from which the gas issues, being brought under the edge of the jar, which is generally sustained upon a shelf, the water descends according as the bubbles of gas ascend; and when the jar in the water has been all replaced by the gas, the jar may be removed on a tray, containing as much water as serves to prevent all communication from the interior with the external air.

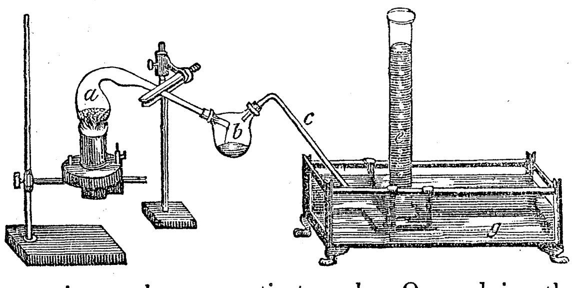


The gasometer, or gas-holder, consists of a cylindrical copper vessel, on which another is secured by five props of copper, of which two are hollow tubes, in connexion with the cylinder below. The tube *m* passes down nearly to the bottom of the cylinder, but the other, *n*, only extends to the upper surface; both are provided with stopcocks, so that the communication between the cylinder and the upper vessel may be opened or cut off at pleasure. At *l* there is also a small tube with a stopcock, and below there is a large orifice at *i*, which can be tightly closed by means of a screw-plug.

To fill the cylinder with water, the orifice *i* is to be closed, and all the stopcocks, *m*, *n*, *l*, left open. Water being then poured into the upper vessel, it flows in through the tubes *m* and *n*, while the air issues at *l*. When water begins to flow out at *l*, that stopcock is to be closed, and then the air which still remains escapes by the tube *n*, bubbling through the water in the upper vessel. When this also ceases, the stopcocks *m* and *n* are to be closed, and the orifice *i* being then opened, the cylinder remains full of water by the external pressure. The tube from which the gas issues is inserted at *i*, and a quantity of water escapes by that aperture equal in volume to the gas which passes in.

A great variety of processes may be put in practice for the purpose of obtaining oxygen gas; one, which is very simple in theory, and of great interest in history, from being that by which the important agencies of oxygen in chemistry were first recognised, although it is not at present practicably useful, is the following:

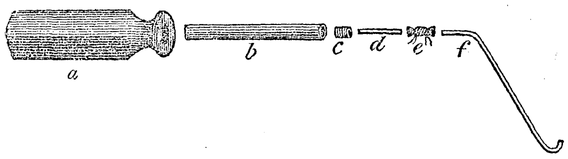
Some red oxide of mercury (Hg.O.) is to be introduced into a retort, *a*, of hard glass, to which is then attached a receiver, *b*, with



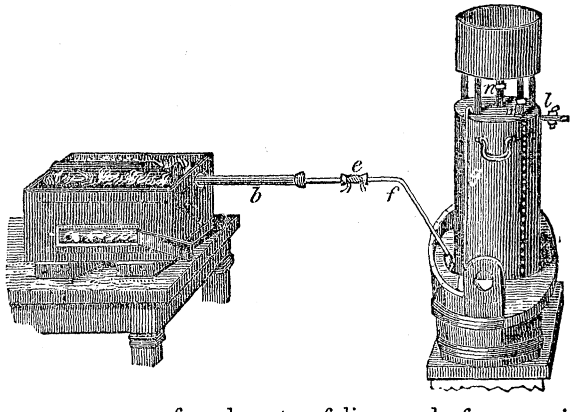
a tube, *c*, passing to the pneumatic trough. On applying the heat of the argand spirit-lamp to the oxide of mercury, it is decomposed; the oxygen is given off in the state of gas, and may be collected in the bell glass *e*, and the mercury distils over, and, condensing in the neck of the retort, collects in drops which flow into the receiver. The substance used is thus resolved into mercury and oxygen; from 109·4 grains, there would have been obtained 101·4 grains of metallic mercury, and 8 grains of oxygen gas, occupying at the standard temperature and pressure 23·4 cubic inches. It was by an

experiment of this kind that Lavoisier demonstrated the true constitution of the metallic oxides.

Although there are few metallic oxides which, as that of mercury, admit of being resolved by heat completely into free metal and oxygen, yet many, when heated, give off a portion of their oxygen, the metal remaining in a lower degree of oxidation. Of this kind are the peroxides of lead and of manganese; and it is generally from the latter that oxygen is obtained for experimental purposes, when it is not required to be absolutely pure. The peroxide of manganese ($Mn.O_2$) abandons, when at a red heat, one third of its oxygen, and a complex oxide, Mn_3O_4, remains, analogous to the black magnetic oxide of iron, and formed by the union of equivalents of pro



toxide and of sesquioxide ($Mn.O.+Mn_2O_3$). For this purpose the manganese is introduced in an iron bottle, *a*, to the neck of which is attached a piece of gun-barrel, *b*, and this connected by a cork, *c*, with a smaller tube, *d*. For sake of freedom of motion, the tube *f*, which passes to the pneumatic trough or the gasometer, is attached to *d* by a caoutchouc connector, *e*. The bottle having been filled about two thirds with oxide of manganese, may be placed either in a common fire or in a furnace, its parts being all arranged as in the figure. When first heated some water passes off, and frequently,

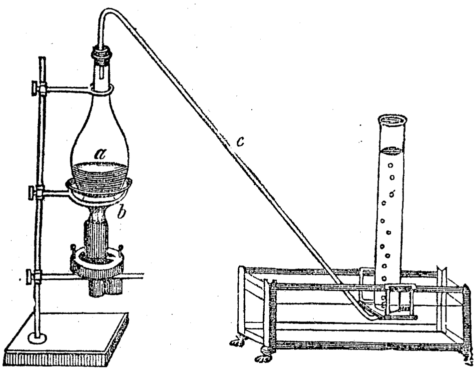


from the occurrence of carbonate of lime and of ammonia in the substance, the first portions of gas are mixed with carbonic acid or with nitrogen; these should be allowed to pass away, and the oxygen collected only when a small tube full of it is capable of relighting a taper four or five times. The pure dry oxide of manganese consists of 27·7 of manganese, united to sixteen of oxygen, of which 5·3 are given off, and hence 1 lb. troy of it is capable of furnishing about 700 grains, or nearly 2000 cubic inches, equal to seven impe

rial gallons of gas. The oxide of manganese found in commerce is, however, not pure; in general it does not contain more than 65 per cent. of pure oxide, and hence the quantity of oxygen furnished by a pound of it is about two thirds only of that just stated.

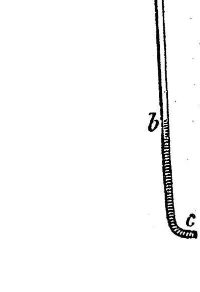
Peroxide of manganese yields more of its oxygen when treated with oil of vitriol than when simply ignited, one half becoming free, while the manganese, with the remainder, forms protoxide, which combines with the sulphuric acid thus: $H.O..S.O_3+Mn.O_2=H.O..S.O_3.Mn.O.+O$.

This operation is conducted by placing the manganese in a flask, *a*, supported in a little cup of sand, *b*, over a lamp, and mixing it with twice its weight of oil of vitriol; a tube, *c*, bent, as in the figure, passes to the pneumatic trough, and dips under the edge of the jar in which the gas is to be collected. When the flask is heated, oxygen gas is rapidly disengaged, but care must be taken that, towards the close, the water of the trough may not pass back into the flask, where, mixing with the hot oil of vitriol, it might produce an unpleasant explosion.



The decomposition which here occurs has been supposed to consist simply in the expulsion of the second atom of oxygen by the sulphuric acid which takes its place. This, however, is not the case. By a very gentle heat, the sulphuric acid decomposes the peroxide, $Mn.O_2$, into protoxide, $Mn.O.$, and permanganic acid, Mn_2O_7 ($5Mn.O_2=3Mn.O.+Mn_2O_7$). This last is decomposed, when the temperature rises, into $2(Mn.O_3)$, manganic acid, giving out one equivalent of oxygen; but the temperature must be raised very much to complete the separation of the $Mn.O_3$ into O_2 and $Mn.O$. Hence, in this process, as ordinarily conducted, the residue in the flask is found to be green, from manganic acid; and, although in theory a more abundant source of oxygen than that by simple ignition, in the proportion of 3 to 2, it is not so useful in practice.

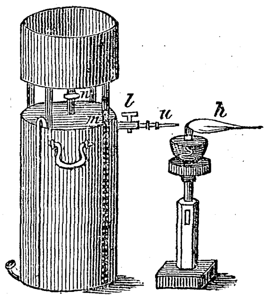
When oxygen is required completely pure, it is generally prepared by heating in a glass tube or flask, to which a bent tube is attached, as in the figure, a small quantity of chlorate of potash. This salt consists of chloric acid united to potash $Cl.O_5+K.O.$, and when heated somewhat above its melting point, it is decomposed, all the oxygen it contains being evolved in the state of gas, and the other elements remaining combined as chloride of potassium. The constituents of this salt are by weight 35·4 chlorine, 39·7 potassium, and 48 of oxygen. Hence 100 parts of it give 39 of oxygen by weight, or an ounce troy, 187 grains,



or 543 cubic inches. An ounce of it is therefore equivalent in effect to six ounces of ordinary peroxide of manganese.

The most remarkable property of oxygen is the energy with which it supports combustion. If a lighted taper be blown out, so that a point of the wick shall continue red, it will be brilliantly relighted on being plunged into a vessel of oxygen gas, and this may be repeated several times in succession. A bit of charcoal, heated to redness at a single point, burns, when immersed in oxygen, with rapid scintillations of exceeding brilliancy; and when phosphorus is inflamed in oxygen, the splendour of the combustion is insupportable to the eye. Even bodies which are not combustible under ordinary circumstances, may be made to burn in oxygen. Thus, if an iron wire be tipped at its extremity with sulphur, or have attached to it a small bit of waxed cotton wick, on lighting this, and plunging the whole into the gas, the combustion extends from the sulphur or wick to the iron, which is converted into oxide, with the disengagement of most brilliant light. The heat evolved by the combination of the oxygen and iron is so great, that the oxide formed is melted, and flows down in drops from the extremity of the burning wire, which, even after having passed through a layer of water, fuse themselves into the substance of the earthenware plate, upon which the gas jar generally stands. If, at the moment when a drop of oxide is about to fall, it be projected by a little jerk against the side of the glass, it will melt its way into its substance, or even, if it be not thick, pass completely through.

The heat evolved when the body burns in pure oxygen may be readily shown by simple methods. If a jet, *u*, be attached to the lateral stopcock, *l*, of the gasometer, and the flame of a spirit-lamp, *h*, be urged by the issuing stream of gas, as by a blowpipe, the most refractory substances may be fused by it. If the tube be curved downward, the jet may be brought to bear on a little cup of red-hot charcoal, in which the body to be fused may be laid, and thus, upon a small scale, the construction and effect of the most powerful wind furnaces may be imitated.



Oxygen gas is necessary to the support of animal life. It is the oxygen which exists in the atmospheric air that fits it for its uses in the economy of nature. The blood which returns dark and venous into the lungs is there changed into the bright arterial state, by absorbing oxygen and evolving carbonic acid, in a manner of which the exact details will be hereafter studied. This change occurs even with blood which has been removed from the body. If a quantity of dark blood, drawn from a vein, be agitated in a vessel of oxygen gas, it is immediately changed into the vermilion-coloured arterial blood. An animal can live longer in a vessel of pure oxygen than in the same volume of atmospheric air; but still, pure oxygen is not fitted for the support of life. It is too stimulating; the animal lives too fast, and ultimately dies with symptoms of general inflammatory fever, even though there may remain still a quantity of oxygen gas capable of supporting the life of another animal for a considerable time.

The name of oxygen was given to this body from the idea of its

peculiar power of conferring acid properties on its compounds; and, in reality, most of the bodies recognised by chemists among the class of acids contain oxygen. But this is not invariable; other simple bodies possess the same power, as has been already noticed on more than one occasion, and I shall have opportunities of recurring to it when describing the properties of those bodies.

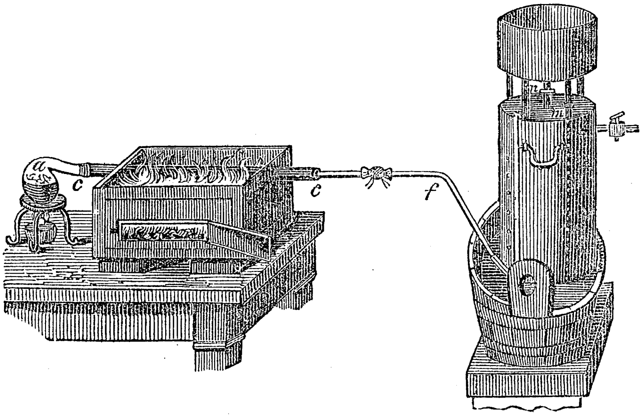
Of Hydrogen.

Hydrogen exists abundantly in nature as a constituent of animal and vegetable substances, and is particularly of interest by forming a constituent of water. From this fact it derives its name, υδωρ γενναω (I form water), and it is by the decomposition of water that hydrogen is almost always obtained for experimental purposes.

If a small quantity of the metal potassium be placed in contact with water, it immediately abstracts the oxygen, forming potash, which is an oxide of potassium. The hydrogen is set free, and appears as a gas. If the experiment be performed under a bell glass, inverted in a basin of mercury or water, the gas may be collected; but if the decomposition takes place in contact with the atmospheric air, so much heat is evolved by the rapidity and intensity of the action, that the hydrogen takes fire, and burns according as it is produced. This is the simplest form under which the decomposition of water can be exhibited, the reaction being $K.+H.O.=K.O.+H.$

If the circuit of the electrical current from a voltaic battery be completed through water, which has been rendered a good conductor by the addition of sulphuric acid, or common or Glauber salt, the two constituents of the water are evolved at the opposite electrodes, or terminating surfaces of the liquid, and the two gases may be collected either separately or mixed together, and will be then found to have been evolved in such proportions that the hydrogen will be double the volume of the oxygen. The theory of this mode of obtaining hydrogen has been described, so far as we are competent to explain it, in a former chapter.

These methods, although the simplest, are yet not applicable to ordinary purposes, from their expense; those usually employed are the following. There are many metals which, although having a powerful affinity for oxygen, are yet not able to abstract it from hydrogen, and so to decompose water at ordinary temperatures; but at a red heat the decomposition rapidly takes place. For this purpose iron is generally employed. A gun-barrel, or an iron tube, *c c*, is taken, and the interior having been loosely filled with iron turnings or coils of iron wire, it is placed horizontally in a furnace, by means of which it can be brought to a full red heat. To one extremity of the tube is connected a small glass retort, *a*, containing water; to the other, a flexible metal tube, *f*, which passes under the shelf of the pneumatic trough. The iron tube being red hot, the water in the retort is made to boil; the vapour passes into the tube, and comes into contact with the red-hot iron; decomposition immediately occurs, and the iron is oxidized, while the hydrogen gas is disengaged in large quantity. The state of combination into which the iron is found to have passed is that of the black oxide, such as the

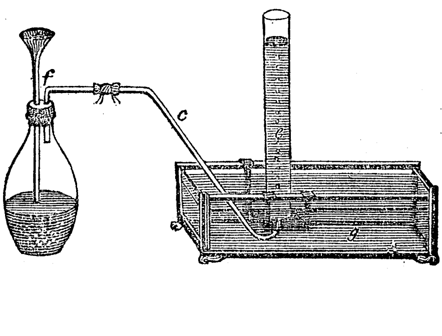


scales that are formed at the smith's forge by the action of the atmospheric air on iron, and which is also formed when iron is burned in oxygen gas. The action may, however, be simply represented as follows:

$$\text{Fe.}+\text{H.O.}=\text{H.}+\text{Fe.O.}\ \text{Protoxide of iron.}$$
$$2\text{Fe.}+3\text{H.O.}=3\text{H.}+\text{Fe}_2\text{O}_3\ \text{Peroxide of iron.}$$
$$3\text{Fe.}+4\text{H.O.}=4\text{H.}+\text{Fe}_3\text{O}_4\ \text{Black oxide of iron.}$$

The action of the iron in thus decomposing water might appear paradoxical, as it will be seen hereafter that by means of a current of hydrogen gas, acting at a red heat, oxide of iron may be decomposed, the iron separating in the metallic state, and water being produced; and thus, at the same temperature, two decompositions, precisely the reverse of each other, may go on. It would appear that this is one of those cases in which affinities, nearly equal otherwise, are directed to one or the other object, according as one or the other substance is in excess. When the iron is kept in a stream of watery vapour, this latter is decomposed, and the hydrogen being carried away, according as it is formed, by the current, it cannot interfere by its presence in any opposing manner. On the other hand, when oxide of iron is heated in a stream of hydrogen gas, it is decomposed, and the water being removed as rapidly as it is produced, the tendency to reaction is prevented.

By the agency of a dilute acid we may also increase the tendency of a metal to combine with water, so that the decomposition of water can be effected rapidly even at common temperatures. If a few slips of zinc or iron be placed in a flask, to which a bent tube, *f*, is adapted, as in the apparatus represented in the figure, and then oil of vitri-



ol, diluted with eight times its weight of water, be poured upon it through the funnel, an abundant effervescence occurs, arising from the escape of hydrogen gas, and the zinc or iron rapidly dissolves. The action continues until the acid has been all neutralized by the zinc, or the zinc all dissolved by the acid; or, finally, until so much of the compound formed during the reaction has been produced, that the water present cannot dissolve any more. This compound consists of oxide of zinc or of iron united to the sulphuric acid, the oxygen of the decomposed water uniting with the metal, while the hydrogen is set free. The process may be thus represented, zinc being used, $Zn.+S.O_3+H.O.=H.+(S.O_3+Zn.O.)$

To account for the circumstances of this reaction, a peculiar power was at one time supposed to exist, termed disposing affinity; and it was said that the presence of the sulphuric acid disposed the zinc to decompose the water, because the oxide of zinc, when formed by the decomposition, might unite with the acid. This theory is quite futile. There can be no oxide of zinc to influence the acid until the water has been decomposed, and the effect, the source of which was to be sought for, had consequently passed away. It appears to me that the explanation is of a much simpler form. Zinc and iron decompose water at ordinary temperatures, even without the presence of any acid, but with excessive slowness, so that the effect is almost imperceptible. In fact, the first minute trace of oxide which is formed, being insoluble in water, coats over the metallic surface with a varnish impermeable to the fluid, and thus prevents its farther action. This coating of metallic oxide is soluble in acids; and thus, by the presence of an acid, a fresh surface of bright metal is kept constantly exposed, and the decomposing action is allowed to proceed without hinderance. It is possible, however, that this simple view may require some alteration, and that this mode of obtaining hydrogen gas may be found to involve voltaic conditions which at present are not well understood. Pure zinc is but very feebly acted on even by a diluted acid; and the rapid action which occurs with commercial zinc or iron may be referred to decomposition by the electric currents which circulate from one portion of the impure metal to the other, through the liquid. See page 135.

Hydrogen gas, when it has been prepared by any of these processes, is seldom pure. The iron and zinc of commerce contain generally traces of carbon, of sulphur, and sometimes of arsenic, which, combining with some hydrogen, form gaseous or volatile products, which give to the hydrogen a peculiar disagreeable odour, and colour its flame. Occasionally, also, traces of potassium and zinc, in very minute division, are carried up with the hydrogen by the mechanical force of the effervescence, but by repose these latter impurities are found completely to separate. To get rid of the former class of impurities, the gas may be made to bubble very slowly through solutions of potash and of corrosive sublimate, by which the arsenic and sulphur would be absorbed, and through alcohol, which would for the most part dissolve the carburetted hydrogen. It is, however, better, when pure hydrogen is required, to prepare it by acting upon water with metallic sodium mixed with quicksilver, so as to moderate the rapidity of the decomposition. Zinc, which

has been refined by distillation, gives also, with sulphuric acid and water, a gas almost completely pure.

When free from foreign matters, hydrogen gas burns with a very pale white flame, almost invisible in bright day. In burning, it combines with the oxygen of the air, and forms water. If a jar of hydrogen gas be suddenly turned with the orifice upward, and inflamed, the whole mass of gas rushes out, and gives a sheet of pale white or yellowish flame. If it be mixed with air previous to being set on fire, the combustion of the mixture is instantaneous, and accompanied with an explosive report. The proper proportions are two volumes of hydrogen gas to five of air. If a lighted taper be plunged into a jar of hydrogen, it is immediately extinguished, the gas not being able to support combustion.

Hydrogen gas is colourless and transparent; it is absorbed by water in very small quantity, and hence, for ordinary purposes, is always collected over that liquid. It refracts light strongly, its refractive index being 6·61, air being 1·00. In its capacity for heat it exceeds all other gases, being 21·9 by Apjohn's experiments, air being 1·00 for equal weights, or 1·46 for equal volumes. It is the lightest substance known, being only one fifteenth of the specific gravity of air; or, more accurately, its specific gravity is 68·8, air being 1000·0.

It is hence used for filling balloons; as the balloon full of hydrogen weighs less than the same volume of air, it ascends with a force equal to the difference of weight. For the purpose of illustrating this property of hydrogen, a small balloon made of gold-beater's skin, or of the serous membrane of the turkey's craw, may be made use of. On this minute scale, however, the gas should be used dry, as, when prepared and collected over water, its specific gravity may be so much increased by the watery vapour it may contain, that, although good enough for a larger balloon, it could not carry up a small one, the small balloon being really much heavier in proportion to the quantity of gas it can contain; consequently, the hydrogen should be dried, which may be effected by causing it to stream from the gasometer through a tube filled with fragments of fused chloride of calcium, which absorbs water with great avidity, and from thence to enter the balloon. At present, hydrogen gas is but seldom employed, it being found cheaper to make the balloon very large, and to use coal gas, which, although much heavier than hydrogen, is considerably lighter than atmospheric air under the same volume.

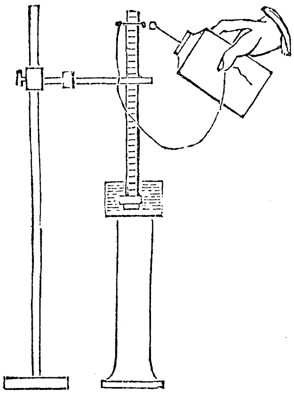
By the same experiment, the three most remarkable properties of hydrogen may be exhibited in an interesting form. If a jar of hydrogen be held vertically, with the orifice downward and open, it will remain filled by the hydrogen for a certain time, as the air, being so much heavier, mixes itself with the lighter gas but very slowly. If a lighted taper be now applied, the gas will inflame at the surface where it is in contact with the atmosphere, but, on plunging the taper upward into the pure gas, it will be extinguished; being then lowered, it can be relighted at the sheet of flame which marks the surface of contact of the gas and the atmosphere, and when again raised into the pure gas, it will again be extinguished; this can be repeated very often: the horizontal sheet of flame having been gradually rising into the jar according as the hydrogen consumed, if then the jar be suddenly turned with the orifice directed upward, the residual gas will at once rush out, and, mixing with the air, will burn explosively with a single flash.

The same experiments on the combustion of hydrogen may be made with pure oxygen gas in place of atmospheric air, but then the results are at least five times more brilliant. The proportions for burning hydrogen with oxygen gas are two volumes of hydrogen and one of oxygen; then, if the gases were pure, nothing but pure water should remain.

If a bladder be filled with the two gases mixed in these proportions, and being punctured, the flame of a taper be applied to the orifice, the whole explodes with a flash of brilliant light and deafening explosion, the strongest bladder being torn to shreds by the expansive force of the ignited gases. In this experiment the bladder

must, of course, be secured, which is easily done by tying the stopcock by which the gas has been passed into the bladder between two nails, with some stout cord or copper wire.

A mixture of hydrogen and oxygen may also be exploded by means of the electric spark; for this purpose a strong tube, closed at the top, and graduated into parts of a cubic inch, is taken, and two brass or platina wires are inserted through the opposite sides near the top, their extremities being kept about one eighth of an inch asunder. This tube is termed a eudiometer, as it is frequently used to measure the quantity of oxygen in the atmosphere, and generally for the analysis of gaseous mixtures. The oxygen and hydrogen gases being confined in this tube over water or mercury, an electric spark is passed through the mixture by means of the wires; the gases explode, and, if the proportions had been accurately observed, no residue is found; if one or the other gas had been in excess, the excess remains behind, one third of the volume which disappears being oxygen, and the other two thirds being hydrogen. In order to explode a bladder full of the mixed gases by means of electricity, a very simple plan is to fasten the bladder upon a large cork, having in the centre an opening, into which a stopcock is screwed for the passage of the gas, and through which, near the edges, pass two stout brass wires, terminating inside the bladder in small knobs; these ends being brought near each other, and the external ends being connected by long wires with the coatings of a charged Leyden jar, the spark passes between the terminal knobs in the bladder, and the explosion immediately occurs.



Hydrogen and oxygen are capable of entering into combination, and forming water without any explosion or visible combustion. If the mixed gases be transmitted through a tube heated to scarcely visible redness, they quietly combine, and this effect occurs at a still lower temperature, if the tube contains coarsely-powdered glass or sand. Slips of gold and silver are still more favourable; but the most rapid union is effected, even at ordinary temperatures, by platinum. This effect appears to be due to the metallic surface retaining a thin layer of gas by so strong a force as by condensation to bring the molecules within the sphere of their mutual chemical attraction; they, combining, form water, and a new quantity of the gaseous mixture comes into contact with the platinum, and follows the same course. If the platinum be in the form of a sponge, in which the acting surfaces are very great, the union takes place so rapidly, that the heat evolved raises the temperature of the platinum ball to bright redness, and then the remaining gas explodes. Platinum in form of sponge always contains a quantity of air in this condensed condition, and hence, when a jet of hydrogen gas is caused to play upon a morsel of spongy platina, it is absorbed, and water being formed, the ball of platinum becomes red hot, and inflames the jet of gas. This constitutes a sort of lamp for instantaneous light, equally pretty and ingenious, the jet of hydrogen in its turn being contrived to fall upon and light a little lamp. See p. 179 and 235.

Spongy platinum introduced into a mixture of oxygen and hydrogen explodes them instantly, but it can be usefully diluted, as it were, by being made into balls with a little pipe-clay, and then it can only produce their union in the slow and silent way. This mode is accordingly often used in the analysis of mixtures of gases, and

tne energy of the platinum balls can be graduated by the proportions of metal and of pipe-clay which are employed. Hydrogen and oxygen, however, are not the only gases which can be made to unite by the agency of platinum surfaces, as will be elsewhere shown.

The heat produced by the combustion of oxygen and hydrogen gases is the most intense that can be obtained by any artificial means. It is hence, at present, much used in an instrument termed the hydro-oxygen blowpipe. The apparatus employed must be of such a nature as to prevent any risk of injury from explosion, which, with any large quantity of the gases, might produce most serious accidents. The safest form for experiment on a large scale consists in having the gases separate, in two gasometers connected by tubes, and of such a size and pressure as that in the same time there will be delivered two volumes of hydrogen to one of oxygen gas. The hydrogen gas tube terminates in a hollow cylindrical jet, inside of which passes the jet of oxygen gas; the flame thus produced resembling that of a candle, into the interior of which is injected a stream of air by the blowpipe in common use. Another form consists of a metallic box, made so exceedingly strong that, even were the gases to explode within it, there could be no danger of its being burst. The gases, previously mixed in a bladder, are forced, by means of a condensing syringe, into the box, and a sufficient quantity having been introduced, the condensing syringe is removed, and a stopcock connected with a jet opened. The pressure of the condensed gas inside forces out a stream, which is ignited, and, if the flame be not allowed to burn too long, the rapidity of the current is sufficient to prevent the passage backward of the flame. This form is now, however, almost totally superseded by the very ingenious safety cylinder and jet of Mr. Hemming. It consists of a brass cylinder of about five or six inches long, by three fourths of an inch in diameter, which is filled as closely as possible by a bundle of fine brass wires, into the centre of which a wedge-shaped brass rod is introduced and driven very hard, so as to pack the wires closely. The interstices between the wires form thus a collection of exceedingly minute tubes, through which the gas must pass. To one end of this cylinder is connected a bladder containing the mixed gases; the other end terminates in a jet from which the gas issues; the flame, in passing backward from the jet, must, in its way to the bladder, stream through the metallic cylinder, and then comes into contact with so great a surface, and so large a mass of material which conducts heat rapidly, that the gases are cooled far below the temperature at which their union can occur, and their farther combustion is, of course, prevented.

For experiments upon a small scale, this little apparatus combines the highest qualifications of convenience, security, and simplicity.

In the flame of the hydro-oxygen blowpipe, the most infusible substances are melted; flint, pipe-clay, the most refractory metals, as platinum, not merely fuse, but even appear to evaporate: a rod of iron takes fire, and burns with a brilliancy surpassing that of its combustion in oxygen gas. Some of the earths alone, are capable of resisting its highest power. These, as lime and magnesia, particularly the former, become, in the flame of the mixed gases, so

brightly luminous as to rival in intensity the noonday sun, and hence furnish one of the most important uses of the blowpipe, by serving for optical purposes as a substitute for the solar ray, which, in our climate, is so uncertain in its supply. The solar microscope fitted up with a ball of lime, ignited by a jet of the mixed gases in place of the solar rays, constitutes the hydro-oxygen microscope, now a common exhibition in our large towns; and the same light has been proposed for use in lighthouses, and has been actually employed for signals in connecting the trigonometrical surveys of the British islands. In one case the light emitted by the ball of lime was distinctly visible at a distance of seventy miles.

A singular phenomenon, which is best produced by the flame of hydrogen, although not peculiar to it, is the production of musical sounds, if an open tube be held over the flame. The flame, in fact, although uniform to the eye, consists of a succession of little explosions of mixed air and gas, which recur too rapidly to be individually distinguishable. If the tube be now held over the flame, it will be seen to flicker, and after a few irregular, interrupted, explosive sounds, a distinct musical note is heard. The explosions set the air in the tube to vibrate, at first irregularly, but at last with such a velocity of vibration as corresponds to the length of the tube, and to the rapidity with which the explosive mixtures of air and gas can be formed; and thus, by any of the known methods of determining the number of vibrations corresponding to a given note, the frequency of the little explosions may be found. Occasionally, also, a distinct beat, or alternations of sound and silence, may be heard, as in two organs, which being nearly, but not completely in unison, sound together; this arises from a current of hot air ascending in the centre of the tube, while a current of cold air is formed next the side. These do not, for a time, vibrate completely as one mass; and hence, at certain periods, alternately redouble and destroy the sounds which they produce.

In its relation to other bodies, hydrogen plays a very remarkable and peculiar part. It was at one time supposed that it shared with oxygen the power of generating acids; and as sulphur, chlorine, cyanogen, iodine, &c., form one class of acids by combining with oxygen, so they formed a second class, called hydracids, by entering into union with hydrogen; and hydrogen was believed to be related to hydrochloric acid, as oxygen was to the sulphuric or the phosphoric acids. In the year 1832, I proved that this view was totally incorrect, and that all the properties of the compounds of hydrogen combined to show that it was an eminently electro-positive body; that it took a place along with iron, manganese, and zinc; and that the compounds of hydrogen with chlorine, oxygen, iodine, and sulphur were almost universally electro-positive in combination, and possessed basic characters derived from the pre-eminent positive energies of the hydrogen itself. These views have, since that period, been still farther corroborated by the researches of Graham, and by additional investigations of my own; and although the old familiar nomenclature will still retain its place to a great extent, yet there rests now no doubt upon the minds of philosophical chemists, that hydrogen is most closely allied to the metals, particularly to zinc and copper; that the chlorides, iodides, and fluorides of hydrogen, although they simulate some of the characters which we assign to acids, resemble, in all important points, the chlorides, iodides, &c., of the metals above mentioned; that, in fact, hydrogen is a metal enormously volatile, standing probably in the same relation to mercury that mercury does to platinum in that respect, but still possessed of all truly chemical peculiarities of the metallic state, and no more de-

prived of the commonplace qualities of lustre, hardness, or brilliancy, than is the mercurial atmosphere which fills the apparently empty top of the tube of a barometer, or the salivating atmosphere of a quicksilver mine or of a gilder's workshop.

Of Water—Oxide of Hydrogen.

H.O.

It has been already shown that water consists of hydrogen and oxygen combined, in the proportions of two volumes of the former gas to one volume of the latter, and by weight of one part of hydrogen united to eight of oxygen, or of 11·1 hydrogen and 88·9 of oxygen in 100 parts.

The exact determination of the composition of water is one of the most important investigations in the domain of chemistry, as from the great range of affinities which oxygen and hydrogen exercise, and the variety of compounds into which they respectively enter, the numbers adopted for the combining proportions of almost all other bodies hinge upon those which are employed for the constituents of water. It has, consequently, attracted the attention of many distinguished chemists. But, although the determination of the respective volumes in which the oxygen and hydrogen unite, as determined by Gay Lussac, gave a very accurate result, yet the most positive determination was obtained by Berzelius, with the method now to be described.

A known weight of black oxide of copper is introduced into a glass tube, on which a bulb is blown, and to the extremity of which a flask, containing the materials for generating pure hydrogen gas, is connected. As, however, the hydrogen gas passes off in a damp condition, and thus introducing water might falsify the result, there is interposed a tube containing fragments of fused chloride of calcium, by which the hydrogen gas is completely dried before it comes into contact with the oxide of copper. When the apparatus has been filled with pure dry hydrogen, heat is applied to the bulb containing the black oxide of copper, and, as soon as its temperature has been raised to dull redness, decomposition commences. The oxide of copper becomes glowing red, and then, even if the heat of the lamp be much reduced, the reaction still goes on; the glowing gradually pervades the whole mass, water is formed and condensed on the colder parts of the tube in considerable quantity, and when the reaction is completed, there remains in the bulb a porous mass of pure metallic copper. It is necessary, however, to determine exactly the quantity of water formed: for this purpose, a small tube filled with fragments of fused chloride of calcium is attached to the bulb tube by means of a caoutchouc connector, and the stream of hydrogen gas is allowed to continue through the apparatus until the residual copper has become quite cold, and all traces of water have been carried into the chloride of calcium tube, where it is completely absorbed and retained. The oxide of copper tube having been weighed before and after the experiment, the loss found is the oxygen which has been carried off: the chloride of calcium tube having been also weighed before and after, the gain gives the weight of water formed, and hence the composition of water may easily be calculated, thus:

100 parts of black oxide of copper give
79·85 of metallic copper, and lose
20·15 of oxygen, which form
22·67 of water;

consequently, 22·67 of water consist of

20.15 of oxygen,
2·52 of hydrogen;

or in 100 parts,

88·9 of oxygen,
11·1 of hydrogen.

To determine the combining equivalents of these substances, or, in theoretical language, their atomic weights, it is first necessary to ascertain what grounds there are for deciding on the atomic constitution of water.

It has been already mentioned that at one time equal volumes of all gases were considered to contain the same number of atoms; and hence, as water is formed by the union of one volume of oxygen and two of hydrogen, it was considered by some chemists to consist of one atom of oxygen united to two of hydrogen; therefore, if we take oxygen as the standard of atomic weights, and call its equivalent number 100, the result would be that 88·9 : 11·1 : : 100 : 12·48= weight of two atoms of hydrogen; and hence the atomic weight of hydrogen should be 6·24. To the adoption of this number there are very many objections: 1st, The ground upon which it was first adopted has been proved to be false, as the same volumes of all gases certainly do not contain the same number of chemical atoms; and, although hydrogen enters so much into combination, it is but very rarely that it does so in the proportion of 6·24. Likewise water, in all the modes in which it is capable of combining, does so in a quantity containing 12·48 and not 6·24; and, finally, water in combination allies itself to a variety of metallic oxides, all of which there is the strongest reason for supposing to be composed of one equivalent or atom of the metal united with one of oxygen.

Water is therefore assumed to be composed of an equivalent of each of its constituents; and according as the standard of oxygen or of hydrogen is taken, its atomic weight is

One atom of oxygen	100·00	8
One atom of hydrogen . . .	12·24	1
	112·24	9

Water is colourless, transparent, destitute of taste and smell. If agitated, it solidifies at a temperature of 32° F. (0 Centigrade), but if preserved quiescent, it may be cooled much lower without freezing; if it be then touched or shaken, a portion is immediately converted into ice, and the temperature of the whole is raised to 32°. In freezing, water expands very much, and exerts therein so great a force as to burst the strongest vessels in which it is contained. It is thus that the surfaces of the hardest rocks are gradually crumbled into soil fit for the support of vegetable life; the water perco-

lating into minute crevices and fissures during the warmer months, and, when frozen in winter, breaking down, by repeated and increasing expansive efforts during successive years, the substance of masses which would appear, from compactness and hardness, fitted to withstand the severest effects of time and climate.

The specific gravity of steam, such as it would be at the standard temperature and pressure, is found to be 620·1, atmospheric air being 1000·0. Two volumes of steam contain two of hydrogen and one of oxygen; hence there is a condensation of three volumes to two produced by the union of the gases. The calculated result is thus found:

Two volumes of hydrogen .	$68{\cdot}8 \times 2 =$	137·6
One volume of oxygen	=	1102·6
give two volumes of vapour of water	=	1240·2
hence one volume of vapour of water	=	620·1

In forming steam at 212°, and a pressure of 30 inches mercury, water expands to 1696 times its volume according to the determination of Gay Lussac, which gives almost exactly the proportion of a cubic inch of water forming a cubic foot of steam, which contains 1728 cubic inches.

The solution of gases in water appears to be governed by principles similar to those which regulate the solvent action of water upon solid bodies. In some instances there certainly takes place chemical union, as in the case of muriatic acid gas and ammonia; and in these cases the condensation of the gases by the water is accompanied by the evolution of considerable heat. But in other cases, particularly where the quantity of gas is small, the result appears to be merely a mechanical distribution of the molecules of the gas throughout the mass of the liquid. The following is a table of the quantity of these gases absorbed by water without combination

100 volumes of water at 60° Fahr. and 30 inches bar. absorb of

Sulphuretted hydrogen	253 volumes.
Sulphurous acid	438 "
Chlorine	206 "
Carbonic acid	100 "
Nitrous oxide	76 "
Olefiant gas	12·5 "
Oxygen	3·7 "
Nitrogen } Hydrogen }	1·6 "

The mixture of nitrogen and oxygen, which constitutes the air we breathe, is absorbed by water, and it is to the air thus dissolved that water, in great part, owes its refreshing taste. If water be boiled this air is expelled, and this should be done if it be wished to saturate the water with any other gas, as the power of water to absorb any other gas is remarkably diminished by the presence of even a small quantity of air. If water already saturated with one gas be exposed to the action of a second, it lets a portion of the first escape, and absorbs a corresponding quantity of the second. In this way, a very small quantity of a sparingly soluble gas may expel a large quantity of one much more soluble. A familiar example of this fact consists in taking a glass half full of Champagne, and

having formed the palm of the hand into a hollow cup, to strike the top of the glass, closing the glass and flattening the hand at the same time; the air above the wine is thus forcibly compressed, and a portion is then absorbed, under pressure, by the fluid, from which a quantity of carbonic acid is expelled, greater than that of air absorbed in the proportion of 1060 to 16, and thus the effervescent character of the wine restored.

Notwithstanding this character of neutrality, which renders water so useful as a vehicle or solvent for more energetic bodies, water is actively engaged in a great variety of chemical reactions, in which its elements, separating from one another, appear in an isolated state, or, by combining with other substances which may be present, generate new compounds. Even, however, independent of decomposition, water plays a most important part in chemical theory, from the numerous classes of compounds of which it forms a constituent. The generality of saline bodies, in crystallizing, retain a quantity of water, often more than one half their weight; this is termed water of crystallization. On the application of a moderate heat this water separates, and frequently the salt dissolves in its own water of crystallization on being heated, undergoing what is termed watery fusion.

Salts containing water of crystallization often attract still more if surrounded by damp air, and fall into a liquid state: such are termed deliquescent salts; others, on the contrary, give off their water of crystallization even at ordinary temperatures, if the air be moderately dry; some, such as the carbonate and sulphate of soda, losing all; others, as the phosphate of soda, only a portion of that constituent: these are termed efflorescent salts; when the efflorescence is complete, they lose their crystalline arrangement and fall to powder.

Graham has shown, that in many classes of salts, particularly in the sulphates, one portion of the water is much more intimately united than the remainder; that, in fact, in addition to the mere water of crystallization, which may be removed without injury, there is water essential to the constitution of the salt, and replaced by other bodies when the salt enters into combination. Thus, in the common crystallized sulphate of copper there are five atoms of water, of which four are removable by a temperature of 150°, but the fifth withstands a temperature of 300°. The formula of this salt is, therefore, not $Cu.O..So_3+5H.O.$, but $Cu.O..S.O_3\ H.O.+4H.O.$, the four atoms being water of crystallization; now if this salt be combined with sulphate of potash, this fifth atom of water disappears, and the double salt is $(Cu.O..S.O_3)\ (K.O..S.O_3)\ +4H.O.$; the $K.O.\ S.O_3$ having entered into the place of the water which had been expelled; water thus circumstanced is termed constitutional water, as being necessary to the complete constitution of the substance.

Water, in combination with the stronger acids, is capable of acting as a base, and, indeed, we know of the existence of many acids only in the form of their compounds with water. Thus the nitric, the chloric, the oxalic, the acetic acids, have never been obtained in a separate form; what we generally term those acids being, in reality, compounds of these acids with water—salts of water. Oil

of vitriol is a compound of sulphuric acid and water, sulphate of water, and it combines with more water, producing great heat, to form a sulphate of water with excess of base, precisely as the sulphate of copper combines with more oxide of copper to produce a corresponding basic salt. The salts of water possess the most complete similarity with those of zinc and copper, and it is from their comparative study that the evidence in favour of the view inculcated already, of hydrogen being a volatile metal, has been in greatest part derived.

Water combines also with bases: the majority of metallic oxides combine with water, often with the evolution of considerable heat. The slacking of lime, which is the act of combination of dry lime with water, produces so much heat as to ignite gunpowder, and, when in large quantity, to become red hot. Ships laden with lime have often been burned at sea, from water getting into the hold among the lime, and so much heat being evolved as to set the ship on fire. Barytes and strontia produce, in slacking, still more heat. Potash retains water so strongly that it can only be obtained free from it by the direct combustion of the metal, potassium, in dry oxygen gas or air. In relation to these powerful bases, water appears, therefore, to act the part of a feeble acid.

The compounds of water have been generally termed by chemists hydrates; thus, hydrate of lime, hydrated oxide of copper, hydrated sulphuric acid, hydrated sulphate of zinc. The very different functions performed by water, in the various modes of combination it affects, render it necessary to adopt a definite principle of nomenclature in this respect. In the subsequent pages I shall employ the word *hydrate* only where the water is combined with a base, such as a metallic oxide; thus, hydrate of lime, hydrate of potash, hydrated oxide of lead. Where the water is united to an acid, I shall, in all cases in which the true chemical nature of the compound comes into play, term it a salt; as sulphate of water, oxalate of water, &c.; but where no strict theoretical explanation is involved, I shall continue to use the common name, as oil of vitriol, strong sulphuric acid, oxalic acid, aquafortis, &c. There is no name peculiarly applicable to the form of compounds which contains constitutional water, but it will serve as well to characterize the absence or deprivation of this water by the word *anhydrous*, the ordinary name of the substance being supposed to include the combined water; thus, common sulphate of zinc, freed from water of crystallization, is $Zn.O..S.O_3.H.O.$; anhydrous sulphate of zinc is $Zn.O..S.O_3$.

When there exists water of crystallization in a salt, it is of course included when the salt is spoken of as crystallized. In formulæ, for the purpose of distinguishing between water of crystallization and water more closely united, the latter will always be marked by the symbols of its constituents, the former by the two initial letters of the Latin word *aqua*, aq.; thus the crystallized oxalic acid is $C_2O_3.H.O.+2Aq.$ The phosphate of soda is $P_2O_5+2Na.O..H.O.+24Aq.$

Water does not exist in nature in a perfectly pure condition. It contains dissolved a small portion of atmospheric air and of carbonic acid, and also certain quantities of solid impurities, of which com

mon salt, sulphates and carbonates of lime, and chloride of magnesium, are the most important. In particular localities, the water issuing from the earth contains iron, and often sulphuretted hydrogen; also traces of iodine and bromine; and occasionally the quantity of these foreign matters present is so great as to confer upon the water medicinal properties, and to make such springs, under the name of mineral springs, spas, be resorted to for the purpose of preserving or recovering health. These impurities arise from the water, in percolating through the porous rocky strata, of which the mountains and general crust of the earth are composed, dissolving in small quantity almost all the substances it meets. Hence rain-water or snow-water, collected at a distance from houses, is the purest water which can be obtained in nature. It contains only some carbonic acid and air dissolved. The sea being the general reservoir into which all the rivers of the earth discharge their waters, contains in a concentrated form all the materials which the river waters had carried down. Although not of absolutely the same constitution all over the globe, yet it varies so little that the deviation may be explained by local circumstances. It is in many countries the source from which common salt and sulphate of magnesia are derived. When sea-water freezes, the ice contains scarcely a trace of saline matter, so that, when melted, it forms a sweet, drinkable water. Hence, in voyages in the Northern Seas, supplies of fresh water are obtained by chopping blocks of ice from the frozen surface of the ocean. To obtain water pure for chemical purposes, it is necessary to distil it. The saline and fixed impurities remain behind, the pure water passes over. Its purity may be ascertained by means of the reagents fitted to detect the most important impurities. Thus, if free from common salt, it will give no precipitate with a solution of nitrate of silver; if free from lime, it will not be affected by oxalic acid; and if it be not rendered turbid by nitrate of barytes, it can not contain sulphuric acid.

From the inactivity of water, and the facility with which it may be obtained pure, as well as the important part which it plays in the economy of nature, it is taken as the standard with which the properties of other bodies, when numerically determined, are compared. Thus the specific heats of solids and liquids are reduced to a scale, water being taken as 1·000. The specific gravities of liquids and solids are also taken in numbers, that of water being the standard. If, however, the specific gravities, and heats of gases and vapours were reduced to the standard of water, the fractions by which they should be expressed would be inconveniently small; and hence, for this class of bodies, a better suited standard substance is found in atmospheric air.

Of Oxygenated Water. Peroxide of Hydrogen.

$$H.O.+O., \text{ or } H.O_2.$$

This singular substance was first discovered by Thenard; its preparation is somewhat circuitous and indirect, oxygen and hydrogen not combining with each other directly in any other proportions but those which form water.

For its preparation, peroxide of barium must be first procured; this is prepared

by placing pure barytes (oxide of barium) in a porcelain tube, which is heated to redness in a charcoal furnace, and then a stream of pure oxygen gas passed over it as long as it is absorbed; the barytes absorbs as much more oxygen as it already contained, and from Ba.O. becomes $Ba.O_2$.

This substance may be still more easily prepared by mixing pure barytes with its weight of chlorate of potash, and heating it nearly to redness; when the disengagement of oxygen from the chlorate of potash has set in, the mass becomes glowing red at one point, and this appearance spreads over the whole mass like tinder. The barytes burns, as it were, in the atmosphere of oxygen, and forms the deutoxide of barium. If, then, the residual mass be washed with water, the chloride of potassium, which remains from the chlorate of potash, is dissolved, and the deutoxide of barium, combining with an equivalent of water to form a bulky, white, insoluble hydrate, remains behind, and may be collected on a filter.

The best mode of obtaining peroxide of hydrogen from this substance is that proposed by Pelouze. To dilute hydrofluoric acid (fluoride of hydrogen), the peroxide of barium is added until the acidity of the liquor is completely neutralized. The reaction is very simple; the fluorine combines with the barium, while all the oxygen is transferred to the hydrogen, which the fluoric acid abandons; thus, $H.F.+Ba.O_2=Ba.F.+H.O_2$.

The fluoride of barium is insoluble, and may be collected on a filter along with the excess of peroxide of barium; the liquor contains only pure oxygenated water. Fluosilicic acid, which is cheaper, and more convenient than the fluoric acid, may also be used in this decomposition. The fluosilicate of barium separates as an insoluble white powder, and the peroxide of hydrogen remains dissolved.

Thenard's plan consisted in dissolving the peroxide of barium in dilute muriatic acid, and then precipitating the barytes by sulphuric acid. The muriatic acid which became free was then neutralized by another portion of peroxide of barium, and this again precipitated by sulphuric acid. When the liquor had become strong enough, the free muriatic acid was removed by the cautious addition of sulphate of silver, and the sulphuric acid then evolved was precipitated by the addition of pure barytes, carefully avoiding an excess.

The weak solution of peroxide of hydrogen thus obtained must be placed, along with a capsule of sulphuric acid, under the exhausted receiver of the air-pump. The water being more volatile, evaporates first, and the liquor gradually becomes more concentrated, until, finally, the peroxide of hydrogen remains pure behind. If left too long in the exhausted vessel, it evaporates itself without alteration.

Peroxide of hydrogen is a thick, colourless liquid. Its specific gravity is 1·452. It has a nauseous taste, and irritates the skin. It bleaches and destroys all vegetable colours. Its reactions are generally so violent that it must be diluted with many times its volume of water before they can be accurately observed.

Its most curious property is, that by being put in contact with any one of a great number of solid substances, it is decomposed with great rapidity, being resolved into oxygen and water. Black oxide of manganese is one of the most active. If a little of this substance, in powder, be introduced into strong peroxide of hydrogen, in a graduated tube, over mercury, the latter is decomposed almost explosively, disengaging 475 times its volume of oxygen, the oxide of manganese remaining perfectly unaltered. Platinum, gold, silver, quicksilver, particularly if the metal be in the form of leaf or sponge, produce the same effect; and if the peroxide of hydrogen be put into contact with an oxide of these metals, as oxide of silver, it is not merely decomposed itself, but the oxide is also decomposed, the oxygen and metal both becoming free. In the dark, and with strong peroxide of hydrogen, a flash of light is seen to accompany its decomposition, and the tube becomes red hot. The decomposition of the oxide of silver cannot, however, be referred to the great heat produced, as, even if the peroxide of hydrogen be diluted with fifty times its volume of water, oxide of silver produces complete decomposition, evolution of oxygen, and separation of metallic silver; yet the effervescence is not very energetic, and the liquor does not become sensibly warm to the hand.

With other metals, the oxygen, in place of becoming free, enters into combination, forming an oxide of a higher degree; thus, with the oxides of lead and bismuth there are formed peroxides of those metals; with arsenic there is formed arsenic acid. The animal substances fibrine and albumen, which are so similar in most respects, are distinguished from each other by their action on this body, fibrine decomposing it with rapidity, while albumen is without effect. It is highly probable, that in the decomposition of water by the voltaic pile, some of this compound may

be formed, as the quantity of oxygen collected is frequently smaller than it should be; and a portion of the process of bleaching, by exposing the wetted cloth to the action of light and air, may possibly be carried on by the formation and subsequent decomposition of this substance.

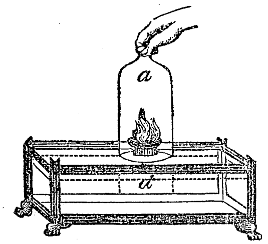
Peroxide of hydrogen, when kept for any length of time, even in a dilute condition, gradually decomposes, oxygen being given off, and water remaining behind. The presence of an acid in the liquor retards this action very much, while the presence of an alkali accelerates it. It was in great part from the remarkable characters of this body that Berzelius derived his evidence in favour of the existence of a catalytic force influencing chemical action, which has been described already.

Of Nitrogen.

N.

It has been already noticed, that the substance by which the oxygen is diluted in atmospheric air, so as to render it suitable to the respiration of animals, is called nitrogen, from its being the basis of nitric acid and nitre (the nitre former). It is also called by some chemists *azote*, from its incapability of supporting life; but, as a great number of gases resemble it in that respect, the former name is the more characteristic, and it alone will be hereafter used.

As nitrogen exists in great quantity in the air we breathe, it is most easily obtained by acting upon a confined portion of the air so as to abstract the oxygen, when the residual gas is found to be nitrogen almost completely pure. Thus, if a small piece of phosphorus, laid in a cup *d*, floating on water, be set on fire, and a bell glass, *a*, be inverted over it, the phosphorus, in burning, unites with the oxygen of the air, and forms white fumes of phosphoric acid. At first, from the great expansion of the air caused by the high temperature of the flame, some bubbles escape from under the edge of the glass; but soon, even before the phosphorus has ceased to burn, the water begins to rise in the bell, and, finally, the clouds of phosphoric acid gradually dissolving in the water, the residual gas will be found to occupy about four fifths of the original volume of the air, and to be colourless as the air had been before. Any other burning body would answer the same purpose, although not so perfectly as the phosphorus. Thus, if spirit of wine, or pyroxylic spirit, or ether, which burn without smoke, be placed in the little cup, and set on fire under the bell glass, as in the former instance, the inflammable constituents, carbon and hydrogen, combine with the oxygen of the air, forming carbonic oxide and water, the nitrogen remaining behind. The gas thus obtained must be washed well with water, or, better, a little solution of potash, to remove the carbonic acid, and even then the nitrogen contains some oxygen unconsumed; for in every case where carbonic acid is formed by a burning body, the combustion ceases before all the oxygen present has been consumed, the carbonic acid exercising on combustion a positively impeding power, similar to that which it has on respiration. The purest nitrogen is consequently obtained by means of phosphorus.

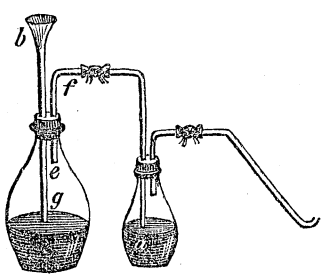


Independent of this source of nitrogen in atmospheric air, it may

be obtained indirectly from a great number of substances. Thus most animal substances contain nitrogen in large quantity, united to carbon, hydrogen, and oxygen. If, therefore, some pieces of muscle, or albumen, or gelatine, be boiled in a retort with some nitric acid, the oxygen of the nitric acid combines with the carbon and hydrogen of the animal substance, forming different compounds according to the temperature and the proportions, while the nitrogen of both is disengaged.

If a gas, termed nitrous oxide, which will be described in a subsequent section, be put into contact with a slip of metallic zinc, at the moment of its formation the zinc deprives it of its oxygen, forming oxide of zinc, and the nitrogen is set free. The apparatus used for this purpose consists of a tubulated retort, into which is introduced the salt (nitrate of ammonia), which, when heated, yields nitrous oxide. Into the tubulure is fitted a cork, through which passes a copper wire, to the end of which a slip of zinc is fastened. To the neck of the retort a bent tube is adapted, passing to the pneumatic trough. Heat being applied to the retort by means of a lamp, the salt melts, and then begins to emit gas. At this moment the copper wire is depressed, so that the slip of zinc may touch the surface of the melted mass. The effervescence immediately becomes much more violent, white clouds of oxide of zinc are formed, and the gas, which passes over, is nitrogen quite pure. The theory of the formation of the nitrous oxide will be noticed under the proper head. Its decomposition by the zinc is simple: nitrous oxide is N. O., and acted on by Zn. their products are N. and Zn.O.

If ammonia dissolved in water be exposed to the action of a current of chlorine, it is decomposed, sal ammoniac is formed, and nitrogen gas is disengaged. The solution of ammonia may be contained in a bottle with a wide neck, *g*, to which a cork is fitted, perforated to admit two tubes, the one, *f*, conveying the chlorine from the vessel *a*, in which it is disengaged, and opening under the surface of the liquid near the bottom, the other projecting but little under the cork, and leading to the pneumatic trough. The action of the chlorine upon the ammonia is accompanied by the formation of white fumes and the evolution of much heat. If the solution be strong, a flash of light is seen at the entrance of each bubble of chlorine gas; but these are not attended with any danger. The ammonia, however, must, all through the process, be kept in excess, as, were the chlorine in excess, it might produce a body, chloride of amidogene, possessed of the most eminently dangerous explosive properties.



The reaction which here takes place may be simply shown. Ammonia consists of one equivalent of nitrogen and three of hydrogen; by the action of three equivalents of chlorine there are formed three of chloride of hydrogen (muriatic acid), which unite then with three equivalents of ammonia to form three of sal ammoniac (muriate of ammonia). Thus (N.+3H.) and 3Cl. give N. and (3Cl.H.), which

combine with $3N.H_3$ to form $3(Cl.H. . N.H_3)$, one equivalent of nitrogen becoming free.

Nitrogen, when obtained by any of these processes, is a permanent gas, colourless and transparent; it is absorbed by water only in very small quantity. It is lighter than atmospheric air, its specific gravity being 976, air being 1000. It is characterized by the complete absence of the positive properties which distinguish other gases. Thus, it does not support combustion or respiration; it extinguishes a taper, and animals are suffocated in it; but these effects appear to be due only to the absence of oxygen.

Although nitrogen is thus incapable of combining directly with oxygen, yet by indirect methods they may be made to unite, and the compounds formed of these elements are surpassed in number and importance by few series of binary combinations. When oxygen and nitrogen combine, their result is almost universally that which contains most oxygen, nitric acid; their union may be effected by the electric spark, provided water, or a solution of an alkali be present; hence rain-water often contains traces of nitric acid, particularly if its deposition has been preceded by discharges of lightning between the clouds; and lime or potash contained in old walls are found, after a certain time, to be neutralized by nitric acid. A mixture of ammonia and oxygen may be converted into nitric acid and water, likewise, by spongy platinum at a temperature of 572°.

The combining proportion of nitrogen is, on the hydrogen scale, 14·0, and on the oxygen scale, 175. In a great number of instances, however, it appears to enter into combination with one third of its ordinary equivalent, and I have found this peculiarity to extend to arsenic and phosphorus, which are so closely assimilated to it throughout their chemical relations.

Before entering upon the history of the compounds of nitrogen with oxygen, I shall describe more particularly the properties and composition of atmospheric air, which, being of so much importance in the majority of chemical reactions which occur on a large scale, and being assumed as the standard of properties for gaseous and vaporous bodies, deserves minute attention.

Of the Atmosphere.

The analysis of atmospheric air was the first important problem in the chemistry of gaseous bodies with which chemists occupied themselves, and hence the names of instruments originally devised for examining atmospheric air became generally used to indicate those employed in the analysis of gaseous mixtures or compounds of any kind. The word *eudiometer* signifies a measurer of the goodness of the air; and from the interest which the problem presented, numerous methods were early invented, although it is only recently that very great precision has been obtained. It was at first believed that the relative salubrities of districts, and even of different localities in the same neighbourhood, could be determined by the proportions of oxygen and nitrogen which the air of these places might contain; and that the admixture of pernicious substances, exhaling from a marsh, or generated within the ill-ventilated apartments of

an hospital or of a jail, might be recognised, and means discovered of removing them, or of destroying their activity, when their nature had become determined by the analysis of the air in which they had been contained. The differences between the results of various chemists, on which these expectations had been founded, have gradually disappeared by the use of better methods, and the constitution of atmospheric air is now recognised as being almost absolutely the same throughout its entire mass; but from other sources, the very results which had been originally sought after now appear to form a legitimate and promising subject of inquiry.

In addition to oxygen and nitrogen, its principal constituents, atmospheric air contains some carbonic acid and watery vapour; the quantity of the latter is determined by methods almost entirely physical, and forms a practical department in the theory of vapours, termed *hygrometry*. I shall, therefore, not touch upon it here, referring to what has been already noticed of it in the sections upon water and upon heat.

The determination of the quantity of carbonic acid present in atmospheric air has been made accurately by Saussure, who found that, in general, 10,000 volumes of air contain 4·15 of carbonic acid; the maximum of carbonic acid he found to be 5·74, and the minimum 3·15. Over the surface of lakes, as that of Geneva, the quantity of carbonic acid is smaller, but in cities greater, amounting to 4·46 in the average: the quantity is somewhat greater by night than by day, and in the higher regions of the air than on the surface of the low ground; it is diminished also during and for some time after rain. To determine the quantity of the carbonic acid, a large globe or bottle containing air is taken, and a solution of barytes is introduced, until, after having been well agitated with the air, it is found, by browning turmeric paper, to be present in excess. The carbonic acid combines with barytes to form a white powder, carbonate of barytes, which, being collected on a filter and weighed, gives, by a simple calculation, the volume of the carbonic acid in the air.

The experiments of Saussure and of Boussingault have made it probable that carbon combined with hydrogen (probably as the gas of marshes) exists in very small quantity in atmospheric air. Thus, when Saussure, after having removed all carbonic acid by barytes, detonated the residual air with pure hydrogen, he obtained a quantity of carbonic acid equal to nearly one part in 2000 of the air employed; and, although employing other methods, the results of Boussingault strongly corroborate the same idea: he found sulphuric acid to be blackened when exposed to air, although all access of dust or accidental impurities was removed, and that when air, previously freed from carbonic acid, was passed over red-hot oxide of copper, a perceptible quantity of water and of carbonic acid was produced.

But the most important portion of the analysis of atmospheric air is to ascertain the proportions of the oxygen and nitrogen. To effect this, any one of a great variety of bodies which are capable of uniting with oxygen may be used; thus, if a solution of sulphuret of potassium be exposed to air, it absorbs oxygen, and gradually passes to the state of hyposulphite of potash, and by the amount of absorption the quantity of oxygen may be ascertained. This is the

method of Scheele. One proposed by Sir Humphrey Davy consisted in agitating the deep olive liquor formed by passing nitric oxide gas into a solution of green sulphate of iron, with a measured quantity of atmospheric air; but it is now abandoned. An excellent mode of using these bodies as eudiometers is to fill with the liquid a small caoutchouc bottle, holding about two fluid ounces, and then tie it securely on the tube of air which passes pretty closely in at the neck; the mass of air and fluid can thus be brought extensively into contact, and the absorption is shown by the gradual rise of the liquid in the tube, the soft parietes of the bottle yielding to the pressure of the external air.

Nitric oxide gas possesses the property of combining with the oxygen of the air, and forming deep red fumes of nitrous acid, which dissolve in water. By this means, using an excess of the nitric oxide, all oxygen may easily be removed from atmospheric air, but the composition of the nitrous acid fumes is not always the same, and hence the quantity of oxygen which the air contained is liable to be mistaken. This mode, therefore, from the great precaution necessary in its use, has been quite laid aside.

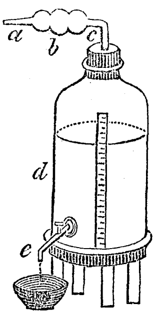
The use of the hydrogen gas eudiometer, whether the combination of that substance with the oxygen be accomplished by the agency of the electric spark, or by means of spongy platina, has been already noticed. It is one of the most accurate and easy methods that can be used, and hence has been most generally employed. The risk of accident from the violence of the explosion by the electric spark is much diminished by using the form proposed by Ure. The tube, which need not be at all so stout as in the common form, is taken about twice as long, and bent into the form of a U. Having been filled with mercury, the mixture of air and hydrogen is transferred to the sealed leg, and then, the open leg being about half occupied by air, it is to be firmly closed by the thumb or by a cork. When the explosion follows, the air in the open leg yields to the pressure and graduates the shock; no portion of the exploded mixture can be projected.

Slips of copper foil, moistened with muriatic acid, absorb oxygen with great avidity, and have been proposed by Gay Lussac for the analysis of atmospheric air. Saussure has used in his accurate researches thin filings or turnings of lead, which combine with oxygen very rapidly, and remove it totally from the air.

Phosphorus, which burns in oxygen and in air so brightly, may also be employed to form a eudiometer. It may be used either by slow or by rapid combustion. In the former mode, a stick of moistened phosphorus, placed in a graduated tube of air, deprives it completely of its oxygen in about twenty hours; the residue is nitrogen, which has the smell of phosphorus, and requires a correction for a small quantity of vapour of that substance which is diffused through it. The rapid combustion of phosphorus is too violent, and exposes the vessels to too much risk of breaking, to be made use of for accurate experiment.

All of these methods are, however, liable to error to the amount of nearly 1 per cent., which is to be in great part attributed to the small quantity of air which the apparatus allows to be experimented

on. This disadvantage has been obviated by the mode proposed by Brunner, and used by him in some determinations lately made, in which the liability to error has been reduced to 0·20 per cent. In the figure, *a*, *b*, *c* is a tube, consisting of a wide portion, *b*, and a narrower, *c*; the wider part being drawn in *a* to a capillary opening. Into it is introduced a quantity of loose cotton and some bits of phosphorus, and being then warmed, the melted phosphorus is allowed to spread over the fibres of the cotton so as to expose a very great surface. The tube at *c* fits air-tight to the orifice of the vessel *d*, which is graduated and filled with mercury; a cock at *e* allows the mercury to flow out on occasion. To use this apparatus, the tube *a*, *b*, *c* is weighed, and then attached to the vessel *d*; the cock *e* is then slightly opened; the mercury issues out in a properly graduated stream, and its place is supplied by air, which, entering at the capillary orifice *a*, streams over the surface of the phosphorus, by which all its oxygen is removed, and the residual nitrogen passing into the graduated vessel, its volume can be easily read off; or the mercury which flows off being caught in a graduated glass, its volume is equal to that of the nitrogen which has passed in. Besides extending the surface of the phosphorus, and thus quickening the absorption of the oxygen, the mass of cotton serves as a filter to collect the white fumes or flakes of phosphorous acid formed. When a sufficient quantity of air has passed through the apparatus, the tube *a*, *b*, *c* is to be weighed again; the increase of weight is the quantity of oxygen absorbed, from which the volume may be known, and the mercury measured is the volume of the nitrogen, from whence its weight may be calculated. The air must be of course dry. This is effected by securing to the tube *a*, *b*, *c*, by means of a caoutchouc connector, a small tube containing fragments of fused chloride of calcium, through which the air streaming deposites the moisture it may contain.



The result of all these methods indicates that atmospheric air contains from 20·79 to 21·08 of oxygen gas in 100 volumes; and from experiments of Gay Lussac on air brought down by him from a height of 21,735 feet, to which he had ascended in a balloon, and those of Brunner for the air on the summit of the Faulhorn, 8020 feet above the level of the sea, the constitution appears to be identical at all heights. By weight, the constituents of the atmospheric air in 100 parts are, omitting carbonic acid and water,

Oxygen gas	=23·04
Nitrogen gas	=76·96
	100·00

This permanency of constitution of atmospheric air, together with many other circumstances which I shall briefly notice, led to the opinion among many chemists of its being a compound, and not a mere mixture of its constituents. The analysis not being then so accurately made, it was supposed to consist of one volume of oxygen united to four volumes of nitrogen, a simplicity of proportion

which characterizes chemical union among gases. It was also remarked, that if the nitrogen and oxygen were merely mixed, their different densities should cause them to separate; the heavier oxygen accumulating near the earth, while the lighter nitrogen should occupy the higher regions of the air. The former ground has been completely disproved by later research, and the elements of air are separated from one another by such feeble means, thus, by nitric oxide, by metallic lead, by agitation with water, &c., as would be unexampled in chemistry among substances of a constitution such as it, if a true compound, should be supposed to have. Besides, its density, its refractive power, its specific heat, are the mean qualities of the oxygen and nitrogen which form it; circumstances which necessarily occur if it be a mixture, but which do not take place in any case of chemical combination. An artificial mixture, also, of oxygen and nitrogen possesses all the properties of atmospheric air.

It is also not the fact that gases of different densities tend, when mixed together, to separate, and form different layers, in accordance with their specific gravities. On the contrary, if two bottles, containing, the one, *a*, a lighter, and the other, *e*, a heavier gas, be connected by stopcocks, *b*, *c*, *d*, and allowed to stand for a few hours, the bottle containing the heavy gas being lowest, they will be found to mix, the lighter gas finding its way to the lower bottle, and the heavy gas ascending to the bottle which is above. In this process the gases evince a positively active power of penetrating into the spaces occupied by each other; and this occurs even when they are separated by membranes, or by masses of porous earthy substances. This peculiar property of gases was first recognised by Döbereiner, and then studied by Mitchell, but finally examined, and its laws accurately assigned, by Graham. When gases of unequal densities are placed in contact with each other, they tend to mix ultimately in a uniform manner; but the rapidity with which they penetrate each other's volume, or, as it is termed by Graham, the velocity of diffusion of the gases, is unequal, and depends upon their densities; the lighter gases diffusing themselves most rapidly, the heavier more slowly. Thus, if a tube be closed at the top by a plug of plaster of Paris, which, when dry, is very porous, and filled with hydrogen gas, the plug being kept dry, the hydrogen and the external air tend to mix across the porous plug; but the hydrogen comes out more rapidly than the air gets in, and hence the water rises considerably in the tube. In a similar way, if a glass be filled with hydrogen gas, and, the top being closed by a sheet of India rubber, a bell glass of air be inverted over it, the hydrogen passing out of the glass more rapidly than air enters to supply its place, the sheet of India rubber is gradually bent into the glass, and ultimately burst by the external pressure. On the contrary, if the small glass contain air and the bell glass hydrogen, the membranous cover is gradually forced upward by means of the excess of hydrogen which passes in, and which finally breaks through it by the elasticity thus produced inside.

The exact law of the diffusion of gases is, that the velocity of diffusion is inversely proportional to the square roots of the specific gravities of the gases. This is exhibited in the following table.

	Specific Gravities.	Square Roots of S. G.	Diffusion Volume
Hydrogen	0·0688	0·2623	457
Ammonia	0·5898	0·7681	130
Air	1·0000	1·0000	100
Carbonic acid	1·5239	1·2345	81
Chlorine	2·4700	1·5716	64

By this table it will be seen, that in the same time in which 100 volumes of atmospheric air escape from a vessel through a membranous or porous plug, 457 volumes of hydrogen pass in; and if the vessel were previously full of hydrogen, 457 volumes will escape from it during the entrance of 100 volumes of atmospheric air. If the vessel contained carbonic acid, the result would be the passage of 81 volumes in the same time, and so of the other gases.

[This law is, however, entirely departed from when the gases are separated from one another by a plug or barrier which exerts upon them a condensing action, and the diffusion volumes are found to be other than those indicated in the foregoing table. A plug of stucco exerts but little condensing effect upon the gases, and hence their diffusion takes place into one another with a velocity inversely proportional to the square roots of their densities; but a thin lamina of India rubber, effecting a powerful condensation, presents the two gases to each other with densities that are abnormal, and hence disturbs their rate of diffusion.

Phenomena of this kind may be very beautifully shown by means of soap-bubbles. If a vial that has had a film of soap-water spread over its mouth be exposed under a jar to an atmosphere of ammonia or protoxide of nitrogen, its horizontality is instantly disturbed, and it begins to assume a spherical convexity, and continues expanding until, after passing through a series of brilliant colours, it may become so thin as to be almost invisible. To show the great rapidity with which a gas or vapour will pass through such barriers, if a soap-bubble be expanded in a vial containing a little aqua ammoniæ, and the air from its interior be immediately withdrawn into the mouth, the strong caustic taste of the ammonia will be immediately perceived.

Through thin pieces of India rubber gases will diffuse into each other, though resisted by any given pressure. I have found that sulphuretted hydrogen will thus pass into atmospheric air against a pressure of more than fifty atmospheres.]

This law of the passage of gases through each other is the same as that for the passage of a gas into a perfectly empty space. If the different gases be allowed to strain through a porous plug into a vessel from which the air has been removed by the air-pump, they will enter with different velocities, regulated by their specific gravities, precisely as in the former instance; and hence it is experimentally demonstrated that different gases are ultimately permeable to each other, precisely as the spaces they occupy would be if entirely empty; that the gases, in fact, form vacua to each other, but that so far as the law of mixture and the final effect are concerned, the mixture taking place more slowly, in consequence of the mechanical obstruction.

This general principle had, however, been laid hold of by the keen intellect of Dalton, and announced long before its truth had been accurately proved in the manner that has been now described; to him we are indebted for the first philosophical view of the molecular constitution of the atmosphere; he proposed to consider the different gases which exist in the atmosphere as being in all points independent of each other, mixed uniformly in virtue of the diffusive power which he had been the first to recognise, and exercising pressures upon the surface of the earth proportional to their quantities. Thus, if we suppose 100 parts of atmospheric air to consist by weight of,

Nitrogen gas	75·88	100·00
Oxygen gas	23·04	
Watery vapour	1·03	
Carbonic acid	·05	

the pressure of the air being taken at thirty inches of mercury, the respective pressures of the independent atmospheres will be as follows:

Pressure of the nitrogen gas	22·764	inches.
" oxygen gas	6·912	"
" watery vapour	0·309	"
" carbonic acid gas	0·015	"
	30·000	

The different constituents of air are thus in the state best suited to the purposes for which the atmosphere is destined; no one gas can interfere with, or retard the others' action; there are no affinities to be overcome, or existing combinations to be broken up, before the agency of watery vapour, of carbonic acid, and of oxygen can be brought into the extended alternations on which the continued and happy existence of animal and vegetable life depends, from which arises the diversity of aspect of our ever varying sky, and the gradual detrition of the solid rocky materials of the earth's surface giving a fruitful soil.

By the processes of combustion and of respiration which are in action on the surface of the earth, the oxygen of the atmosphere is continually removed, and an equal volume of carbonic acid generally substituted for it. This carbonic acid is absolutely a narcotic poison, and the air becomes unfitted for the support of life before one half of the quantity of oxygen it contains has been consumed. A healthy man spoils in twenty-four hours, by respiration, 720 cubic feet of atmospheric air, that is, a mass of air eleven feet square and six feet thick. The burning of three ounces of charcoal produces the same effect. In many factories there are burned daily ten tons of coal, which deteriorate at least as much air as the same weight of charcoal, and hence each day, by such a factory, there is rendered unfit for respiration 3,185,760 cubic yards of air, which would cover to the depth of six feet a space a quarter of a mile square. Nevertheless, it has been already mentioned, that even in cities, the relative proportions of oxygen, nitrogen, and carbonic acid in the air are but little altered, and it becomes an object of great interest to ascertain in what manner that permanency, on which the stability, in truth, of all organized nature seems ultimately to depend, has been secured.

In the first place, from the frequent occurrence of storms and violent currents, which agitate vast tracts of air, accumulation of noxious gases or corrupted portions cannot take place, except in some rare and limited localities, which do not affect the condition of the atmosphere even near at hand; and although the numbers which have been shown as indicating the amount of air destroyed become enormous when multiplied by the number of breathing beings and the quantity of fuel burned on the earth's surface, they yet bear but a trifling proportion to the immensity of the aërial ocean in which we live. The atmosphere may be considered as being, if brought throughout to its usual density at the surface of the earth, about five miles deep; and Prevost has calculated that the loss of all the oxygen employed in respiration and combustion for 100 years could not diminish its quantity by $\frac{1}{7200}$ part, a quantity too trifling to be detected by our methods, even had the exact sciences flourished for such a period as to allow a comparison to be made.

But, independent of this negative proof of permanence of com-

position, science has pointed out, in the peculiar relations of the functions of vegetable and animal beings, a provision of adaptation to each other's wants, which retains the atmosphere in a condition practically of eternal identity of constitution. A healthy growing plant, exposed to sunlight, is found to absorb carbonic acid, and to emit oxygen from the surfaces of its green leaves. In the dark, an inverse effect takes place, oxygen being absorbed, and carbonic acid formed. The coloured parts of plants, as flowers and fruits, absorb likewise oxygen, and emit carbonic acid; but as the green surfaces preponderate so much throughout the vegetable world, and the stimulus of light is active throughout the greater portion of the twenty-four hours, the ultimate effect is, that an action the opposite of that which animals exercise upon the atmosphere is constantly going on. That which the plant rejects is to the animal the source of energy and of all vital powers, while the same element which the plant absorbs, and from which it forms its tissues, has been thrown out as useless by the animal, and would, if not removed, accumulate in the end, and destroy all animal existence.

The most accurate experiments have determined that 100 cubic inches of atmospheric air, freed from moisture and carbonic acid, weigh 31,0117 grains; the barometer being at 30 inches, and the thermometer at 60°. Its specific gravity is taken as the standard for gases and vapours, and is hence 1000. It is about 780 times lighter than water at 40·5° Fahrenheit, when water is at its greatest density, and is then also 10,600 times lighter than quicksilver.

The weight of the atmosphere pressing upon the surface of the earth is equivalent to about fifteen pounds on each square inch of surface. The existence of this pressure may be shown in many ways: a bladder or a thin plate of glass may be burst if the pressure of the air be removed from one side by the air-pump while it is allowed to act against the other; a pair of brass hemispheres, which are easily separated while filled by air, are pressed most firmly together if the air be removed from their interior. This pressure is equivalent to that exercised by a column of mercury in a tube about thirty inches high, and, accordingly, an instrument, the common *barometer*, or pressure measurer, is thus constructed, to register, at every moment, the pressure which the atmosphere exercises. A tube closed at one end, and about thirty-two inches long, is to be carefully filled with pure mercury; it is then inverted in a basin of mercury, and being placed in a vertical position, the column of mercury sinks to a certain height in the tube, generally between twenty-nine and thirty inches, leaving above it a space which is, at low temperatures, the most perfectly empty that can be experimentally procured. From the name of the inventor of this instrument, it is called the Torricellian vacuum. If the external pressure varies, the height of the column of mercury alters likewise, rising when the pressure increases, descending when it is diminished; and as considerable changes in the amount of pressure generally depend on violent motions in the air, which produce changes in the weather also, the barometer is popularly regarded as a weather-glass, although no accurate indications of approaching changes can be at all reckoned on from its use.

If the atmosphere preserved throughout its entire mass the same density and elasticity which it possesses at the surface of the earth, its height would be about five miles. But such is not the case; the lower portions of the air, which press upon the earth, are pressed upon by the portions next over them, these again by those still higher up, so that the amount of pressure, and, consequently, the density of the air, decreases continually as we ascend through its mass. The rate of diminution is even very rapid, forming a geometrical proportion when the heights are taken in an arithmetic series; and on this principle is founded one of the most accurate modes of estimating heights that has been yet discovered. If a barometer be carried to the summit of a mountain, the column of quicksilver will be observed to be shorter than it had been upon the plain, and the difference being marked, the height corresponding to it is determined, from a knowledge of the law just stated. In practice there are corrections depending on temperatures and other causes, to which it is not necessary to allude. So rapid is this diminution of density, that one half of the whole mass of the atmosphere lies within three miles of the surface of the earth, and four fifths of it within eight miles. Hence, in those elevated regions, the lungs receive, even in a deep inspiration, but little oxygen, and the blood not being well arterialized, causes the headaches, lassitude, and faintness which those who ascend high mountains or in balloons feel so severely. The lakes in the mountainous valleys of Switzerland and the Andes are, for the like reason, destitute of fish; the water holds no air dissolved to fit it for their respiration, precisely as one may kill a fish in water by placing it under the receiver of an air-pump and abstracting the atmospheric air.

The question of how far the atmosphere really extends in space, possesses, in relation to the views of the ultimate constitution of matter, already noticed, considerable interest. If the particles of atmospheric air were capable of division to an infinite degree, then the attenuation which occurs in the higher regions of the air should have no limit, and we should look upon all space as occupied by the elements which form our atmosphere, rarefied to an inconceivably great degree, and our earth as having provided itself, in its course through space, with as much of this circumambient matter as, from its attractive power, it was able to keep round it. If, on the other hand, the oxygen and nitrogen of the air consist of molecules of definite form and size, these, being in the gaseous form, are subjected to the simultaneous action of two forces: one, the mutual repulsion which characterizes the gaseous condition, and which causes their elasticity, but which, diminishing with this elasticity, must become very small in the upper strata of our atmosphere; the other, the general attraction of the earth, which, though much inferior at the surface, must, since it diminishes but very little in ascending so far, at a certain point become equal to the former, and then all farther expanding tendency being overcome, the atmosphere should be terminated by a definite surface, similar in form to that of the solid earth, having its tides and currents like those of our great oceans, and from these various fluctuations in its depth, produce the regular variations in the height of the barometer, which, though involved by the irregular motions of much larger amount, have been detected

The amount of refraction proves that the sensible atmosphere does not extend beyond 45 miles; at least, if it exist higher up, it must be so rare as to have no effect in deflecting a ray of light. But other considerations prove that the air does not extend through space. If we had obtained our atmosphere by gathering up, in virtue of our attracting force, the thin air which pervades all space, the other bodies of our system should also possess atmospheres whose densities should represent the masses of the bodies they include. However, exact observation has shown that even the largest bodies of our system possess no atmospheres. A ray of light suffers no bending in its course, although it passes by the edge of Jupiter; yet, from the immense size of that planet, it should have collected round it an atmosphere so dense, that by its refraction a star should become visible to us upon one side of it before it had disappeared at the other. The sun, likewise, the gravitating centre of our system, does not possess a trace of atmosphere sufficient to cause a sensible refraction.

Poisson has recently suggested a view of the constitution of our atmosphere, upon grounds, however, so little connected with experiment that it would not be a subject for notice here, had it not been introduced to the notice of chemists under the sanction of Dumas's eloquent discourses. I will, therefore, briefly describe the theory he has put forward.

The atmosphere, as we ascend, grows colder. The source from which the atmosphere derives its heat is not the sun, but the solid earth; the solar rays passing through the air as they pass through glass and all transparent bodies, without communicating much of their heat. These heating rays are absorbed by the dark and rugged surface of the earth. From this the layer of air next to it derives its warmth, and hence, the farther from the earth the air is taken, the colder it is found to be. Hence, even under the glare of a tropical sun, there exists an elevation where the temperature never rises above 32°, the melting point of ice; above that height all is eternal snow. Farthest from the level of the sea at the equator, being 15,000 feet, this line of perpetual congelation gradually descends, until at the poles it sinks below the surface of the earth. In these countries we have no mountains with perpetual snow, the line of congelation being 6000 feet above the surface.

From this source, also, are derived the various phenomena of fog and cloud, the production of snow, of hail and rain. The vapour forming at the surface of a pond is generated with an elasticity proportional to its temperature; and when the air, thus mixed with vapour, rises to a higher and colder stratum, the elasticity of the vapour is diminished, and a portion separates either as cloud or rain. Thus, if air becomes loaded with vapour at the surface having a temperature of 60°, and, on ascending, it becomes cooled to 40°, the quantity of water separated is thus found:

The elasticity at	60° is	0·524	inch of mercury.
"	40° is	0·263	"
the difference is	. .	0.261	"

But 524 : 261 : : 100 : 49·8, or nearly 50, and hence almost exactly one half of the quantity of vapour carried up is deposited under the form of cloud; in addition to this, another portion of vapour is deposited as liquid water, from the circumstance of the diminution in volume of the mixture of gas and vapour produced by the lowering of its temperature; this is equal to about four per cent., so that there remains as invisible vapour only about forty-six, while fifty-four per cent. are engaged in the production of the cloudy masses. The farther properties of clouds, the circumstances which determine the production of rain, snow, or hail, are of so little reference to chemistry that I shall pass from them without remark.

Reasoning from the principle that all gases may, by suitable reduction of their temperature, be reduced to the solid form, Poisson proposes to consider the atmosphere as being extended above the earth, gradually becoming more attenuated and more cold, until it arrives at a point at which it freezes; there then should be a shell of transparent colourless air-ice, lined on its concave surface with a sea of

liquid oxygen and nitrogen mixed or combined together. From such assumption, Poisson proposes to render the theory of astronomical refractions more definite and exact than it had before been, but those grounds can scarcely be deemed sufficient to justify the adoption of that idea as a physical reality. So far, in fact, as collateral evidence can be found, the fundamental idea of Poisson's theory is disproved; for it results from Fourier's researches on the distribution of Heat, that the temperature of the planetary spaces cannot be below —57° of Fahrenheit, a degree of cold which is met with in Melville Island during winter, and which has been far exceeded by artificial means. At this temperature air shows no sign of even becoming liquid, far less solid; and hence the supposition of such a hollow sphere of frozen air cannot be granted.

Compounds of Nitrogen and Oxygen.

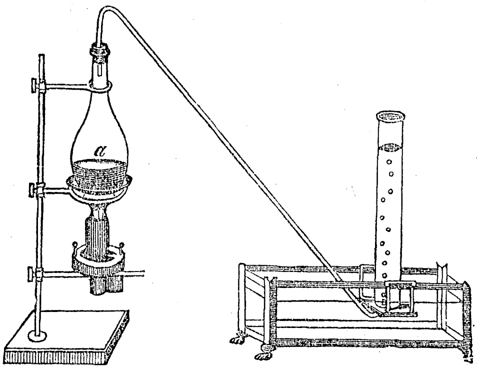
Nitrous oxide . . .	$N.=14{\cdot}0+O.=8=N.O=22{\cdot}0$
Nitric oxide	$N.=14{\cdot}0+2O.=16=N.O_2=30{\cdot}0$
Hyponitrous acid . .	$N.=14{\cdot}0+3O.=24=N.O_3=38{\cdot}0$
Nitrous acid	$N.=14{\cdot}0+4O.=32=N.O_4=46{\cdot}0$
Nitric acid	$N.=14{\cdot}0+5O.=40=N.O_5=54{\cdot}0$

Nitrous Oxide. Protoxide of Nitrogen.

This substance, which exists, under ordinary pressure, in the gaseous form, is best and most easily prepared by heating to about 350° Fah. the crystallized nitrate of ammonia. This salt melts at 300° Fah. into a colourless liquid, without being at all decomposed or losing water; but when the temperature is raised to 350°, a lively effervescence occurs, and the salt is totally resolved into vapour of water and nitrous oxide gas, an equivalent of nitrate of ammonia producing two equivalents of the gas and four of water, thus:

$$N.O_5+N.H_4O.=2(N.O.)+4(H.O.)$$

The nitrate of ammonia may be placed in the flask *a*, imbedded in the little cup of sand. A bent tube conducts the gas evolved to the pneumatic trough, as in the figure, or to the gasometer, if the quantity be large. In this process the temperature should not be allowed to rise beyond the point at which the effervescence is moderately brisk; for when the salt becomes much hotter, the decomposition is tumultuously rapid, and the gas obtained may not be at all pure.



The nitrous oxide gas so obtained is perfectly colourless and transparent; it is absorbed by water in moderate quantity, and hence the water over which it is collected should always be heated to about 90° in order to diminish the loss of gas thus suffered. It is heavier than air, its specific gravity being 1·527.

A lighted taper burns with increased brilliancy in this gas; and if

blown out, may be relighted, provided a pretty large portion of the wick remains bright red. If the gas be mixed with its own volume of hydrogen, it may be inflamed by a taper or by an electric spark, and then burns with a loud explosion. If phosphorus be heated in this gas, it inflames and burns with almost as much brilliancy as in pure oxygen.

In none of these instances does the nitrous oxide enter into combination. It is decomposed by the high temperature of the burning body and the affinity of this last for oxygen, and the combustion is maintained by means of the oxygen which is thus disengaged. After the process is completed, the nitrogen of the nitrous oxide remains free.

In this manner nitrous oxide may be analyzed. If a little bit of potassium or of phosphorus be heated in a measured quantity of the gas until the decomposition is complete, and then the apparatus be cooled to its original temperature, it will be found that a quantity of nitrogen remains exactly equal in volume to the nitrous oxide used, and the quantity of oxygen absorbed is such, that in its gaseous form it had exactly half that volume. The nitrous oxide consists, therefore, of two volumes of nitrogen and one of oxygen condensed to two volumes, and hence its specific gravity may be calculated thus:

Two volumes of nitrogen $976 \times 2 = $	1952·0
One volume of oxygen . . .	1102·6
give two volumes of nitrous oxide	3054·6
and one volume weighs, therefore	1527.3

By weight, the composition of nitrous oxide and its equivalent number on each scale are expressed as follows:

Nitrogen,	63·9	One equivalent,	14·0 or	175
Oxygen,	36·1	"	8·0 "	100
	100·0		22·0	275

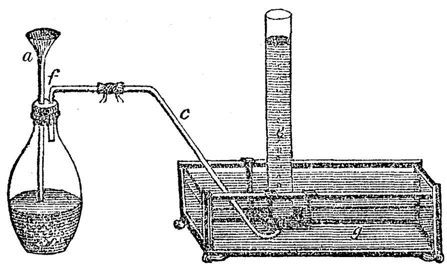
and its formula is N.O.

The most singular property of this gas is, that when breathed pure for a few minutes it produces a lively and agreeable intoxication, which does not leave any lassitude or disagreeable sensation when it goes off. To prepare gas for being breathed, it is necessary to attend to the purity of the nitrate of ammonia used, as very frequently the salt found in commerce contains muriate of ammonia, in which case the gas obtained may be contaminated by nitrous acid and chlorine, and prove very irritating to the lungs. To obtain the full effects of the gas upon the system, four or five quarts must be introduced into an air-tight bag or bladder, and inspired through a pretty wide glass tube. About two ounces of nitrate of ammonia yield sufficient gas to intoxicate one person.

Nitric Oxide. Deutoxide of Nitrogen.

This substance exists naturally under the form of a gas, which chemists have not, as yet, been able to reduce to the liquid form. It is very easily prepared, being almost always the principal product of the decomposition of nitric acid by the metals.

If a small quantity of quicksilver, or of copper cut into small bits, be placed in the gas bottle in the figure, and diluted nitric acid, prepared by mixing equal volumes of the aquafortis of commerce and of water, be poured in by the funnel *a*, effervescence is immediately pro-



duced, even without the application of heat, and the metal dissolves in the acid, which becomes pale green-coloured if quicksilver had been employed, but of a rich blue if copper had been used. From greater economy, the latter metal is almost always that employed. For some time after the action commences, the space in the bottle over the liquid is occupied by reddish fumes; but these gradually pass away, and the gas may be collected when the upper part of the generating flask is occupied by it completely colourless.

The theory of this process is very simple: a quantity of nitric acid gives off three fifths of its oxygen to the copper, and the nitrogen is evolved in combination with the remaining two fifths, forming nitric oxide. The copper, being thus oxidized, combines with another portion of nitric acid to form a fine blue salt, nitrate of copper, which exists in the blue liquor, and may be obtained crystallized. For complete decomposition, four equivalents of nitric acid and three of copper are required, and the action may be then expressed as follows: $4N.O_5$ and $3Cu.$ give $3(N.O_5 . Cu.O.)$ and $(N.O_2)$.

By the action of organic substances, such as starch or sugar, upon nitric acid, nitric oxide may also be formed in abundance, but it is not then so uniformly pure as when obtained by means of mercury or copper.

This gas is colourless and transparent; it is scarcely absorbed by water, and may hence be, on all occasions, collected over it. It is a little heavier than air, its sp. gr. being 1039; its refractive index is 0·8761. A lighted taper plunged into this gas is extinguished, and a red-hot wire may be applied to phosphorus in it without inflaming it; but if the phosphorus be already set on fire, it not only continues to burn when plunged into the nitric oxide gas, but the combustion is almost as brilliant as in pure oxygen. In this case, it is indeed in oxygen, and not in nitric oxide, that the combustion actually occurs; for the gas is decomposed by the high temperature of the burning phosphorus, and, being resolved into its constituents, the oxygen is the body with which the phosphorus combines, and the nitrogen remains untouched.

In this way nitric oxide may be analyzed, and is found to consist of equal volumes of nitrogen and oxygen united without any condensation. From this its specific gravity may be calculated:

One volume of nitrogen . . .	= 976·0
One volume of oxygen . . .	=1102·6
give two volumes of nitric oxide	2078·6
of which one is found to weigh .	1039·3

Its equivalent volume is therefore 4, and its composition by weight and its equivalent number on each scale are as follows:

Nitrogen, 46·95	One equivalent,	=175 or	14·0
Oxygen, 53·05	Two equivalents,	=200 or	16·0
100·00		375	30·0

and its formula is $N.O_2$.

Nitric oxide may be deprived of one half of its oxygen, and so be reduced to the state of nitrous oxide, by remaining in contact for some days with moist iron or zinc filings; in this case its volume is reduced to one half.

The most remarkable property of nitric oxide is its tendency to unite with oxygen when this last is uncombined. Nitric oxide cannot take oxygen from any other substance; but when it is mixed with air, or with any mixture of gases, of which oxygen is one, it unites with this, forming deep red fumes. It is this which causes the red fumes in the flask in which the nitric oxide is generated. The oxygen, in combining with the nitric oxide, may form either hyponitrous acid ($N.O_3$) or nitrous acid ($N.O_4$), and they are both generally formed in uncertain proportions. Hence we cannot exactly calculate the quantity of oxygen that had been present; and this process does not answer well for gaseous analysis, but it is useful for removing oxygen from a gaseous mixture, which it effects completely if the nitric oxide be added in excess. The red fumes so formed are soluble in water, and, by washing the mixed gases with water, may therefore be completely removed.

Nitric oxide combines with a great number of salts and with some acids to form compounds, which in some respects possess considerable interest: these shall be noticed under those heads to which their history more particularly belongs.

Hyponitrous Acid.

The red fumes which are formed when nitric oxide is mixed with atmospheric air or oxygen, consist in great part of hyponitrous acid, particularly when the nitric oxide is in excess. To obtain it pure, four volumes of nitric oxide should be mixed with one volume of oxygen, and the vessel containing the hyponitrous acid vapour formed, exposed to a cold of about 40 degrees below the freezing point of water. The acid then condenses into a deep green-coloured liquid, which is excessively volatile.

When hyponitrous acid, either in the state of liquid or of vapour, is brought into contact with water, it is in great part decomposed, being resolved into nitric oxide and nitric acid, three equivalents of hyponitrous acid ($3N.O_3$) giving $2(N.O_2)$ and $N.O_5$. The same occurs when it is acted on by bases dissolved in water, and hence the salts of this acid can only be prepared by indirect means.

When nitre has been kept melted for some time, so as to have parted with a portion of its oxygen, it is reduced to the state of hyponitrite of potash, $N.O_5 . K.O.$ giving off $2O.$, and leaving $N.O_3 . K.O.$ This is known by the hyponitrite being decomposed by acetic acid, and giving off copious red fumes, while the nitrate of potash is unalterable by acetic acid. The hyponitrite of potash cannot be crystallized so as to free it from the excess of unaltered nitre, but it may be converted into sparingly soluble salts, as those of silver and of lead, and so pure salts of hyponitrous acid formed.

The specific gravity of the vapour of this acid has not been experimentally determined. It consists of two volumes of nitrogen united to three of oxygen, but of their condensation we know nothing.

Its composition by weight and its equivalent constitution are,

Nitrogen,	37·11	One equivalent,	=175 or 14·0
Oxygen,	62·89	Three equivalents,	=300 or 24·0
	100·00		475 38·0

Nitrous Acid. Nitroso-nitric Acid.

This substance presents itself, like the last, under the form of deep red fumes, and is produced when the oxygen is in excess with regard to the nitric oxide. By a cold of about 0° on Fahrenheit's scale, it may be rendered liquid. To form it directly, four volumes of nitric oxide are to be mixed with two volumes of oxygen, and the mixture exposed to a great cold; but it is more conveniently prepared by means of the decomposition of nitrate of lead by heat.

A quantity of finely-powdered and dry nitrate of lead is to be placed in an earthenware or hard glass retort, and heated to full redness. The red vapours that are produced are to be conducted into a receiver, carefully cooled by a mixture of snow and salt. They then condense into a liquid, while a quantity of oxygen gas escapes, and oxide of lead remains behind in the retort. The nitric acid of the nitrate of lead is decomposed into nitrous acid and oxygen, as follows: $N.O_5 . Pb.O.$ gives $Pb.O.$, free $N.O_4$ and O.

The liquid nitrous acid is nearly colourless at zero, at 60° it is orange yellow, and at —40° it solidifies into a white crystalline mass. It boils at 82°, and its vapour, which is ruddy red at that temperature, is almost perfectly black at 212°. In these various coloured states, it exercises remarkable absorbing power on light. The specific gravity of the liquid acid is 1·451.

Nitrous acid is the most stable compound of nitrogen and oxygen; it is not decomposed by a red heat; it is decomposed in great part by water, nitric acid being formed, and nitric oxide being given off as gas. Thus, $3(N.O_4)$ give $N.O_2$ and $2(N.O_5)$. The nitric acid formed always protects a portion of the nitrous acid from this reaction.

When the nitrous acid is formed by the direct union of nitric oxide and oxygen, it is found that the six volumes of gas are condensed by combination into two; hence the specific gravity of nitrous acid vapour should be 3181·2; thus,

One volume of nitrogen	976·0
Two volumes of oxygen	2205·2
One volume of nitrous acid	3181·2

Its composition by weight and the constitution of its equivalent are as follows:

Nitrogen,	=30·33	One equivalent,	=175 or 14·0
Oxygen,	=69.67	Four equivalents,	=400 or 32·0
	100·00		575 46·0

Considerable doubt has been thrown upon the nature of this substance, for many chemists regard it as incapable of uniting with bases, and hence look upon it as a kind of acid salt, consisting of nitric and hyponitrous acids combined together; $2(N.O_4)=N.O_5+N.O_3$. But late researches have shown that it does produce true salts, and that even many saline compounds which had been supposed to be salts of hyponitrous acid really contain this substance; thus, the yellow basic salt, formed by boiling a solution of nitrate of lead on metallic lead, is a true nitrite. I retain, therefore, for this body the old name of nitrous acid, the more as that of peroxide of nitrogen, proposed for it by Graham, is frequently applied to nitric oxide.

Nitric Acid.

$N.O_5$.

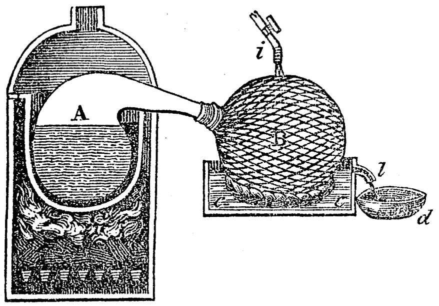
It is found that when nitric oxide is brought into contact with a great excess of oxygen over water, they combine in the proportion of four volumes of the first to three of the second; and when the red fumes which are produced have dissolved in the water, that is found to be a solution of pure nitric acid. Looking to the composition of nitric oxide, we find in this manner that the nitric acid consists of two volumes of nitrogen gas united with five volumes of oxygen.

Although nitrogen and oxygen do not unite at once when directly brought into contact with each other, yet they are capable of combining under certain circumstances; and there is no doubt but that the great, if not the only source of nitric acid in nature, is the union of the nitrogen and oxygen of the atmosphere. Although nitrogen is not strictly inflammable, yet, if some of it be mixed with hydrogen, and this mixture be set on fire, the flame is coloured green, and the water formed is found to contain nitric acid; if a series of electric sparks be passed through a quantity of air confined over a strong solution of potash, this gradually loses its alkaline reaction, and after a time crystals of saltpetre (nitrate of potash) form in it. This may be shown, also, by simply moistening some litmus paper with a solution of an alkali, and taking, by means of it, a succession of sparks from a strong electrical machine; at the point where the spark passes, the paper becomes reddened, and that nitric acid has been formed is shown by its burning like touch paper when dried and set on fire. Rain-water, particularly that which falls after a thunder storm, contains a certain quantity of nitrate of ammonia; the lightning forming, as the electric spark does, nitric acid in passing through the air, and this uniting with the ammonia which is always present in our atmosphere from decomposing animal remains.

In warm climates, where the abundance of organic matter and its rapid decomposition pour into the atmosphere a copious supply of ammonia, the formation of nitric acid proceeds with extraordinary energy, and the nitrate of ammonia being washed down by the rains into the porous limestone soils, the ammonia is again given off, while the ground becomes coated with an efflorescence of earthy nitrates when it dries on the cessation of the rain; a small quantity of nitrate of potash is also thus formed, but the nitrate of lime, of which the crude produce of nitre principally consists, is converted into saltpetre by means of carbonate of potash. In this way there is formed in the East Indies a quantity of nitrate of potash sufficient to supply the wants of Europe. On the Continent, this process is imitated in artificial nitre-beds, and large quantities of home-made saltpetre are used in France and Germany for the manufacture of gunpowder. In South America, particularly in Chili and Peru, there are found immense deposites of nitrate of soda upon the surface of the soil, and it is now extensively imported into these countries; the source of the nitric acid is, in this case also, the union of the elements of the atmosphere, although the circumstances which supplied the alkali cannot be distinctly seen.

It is from the nitrates of soda or potash so produced that the nitric acid is always obtained. True nitric acid has never been isolated; that substance which is generally spoken of as nitric acid, and which I shall, unless especially remarked otherwise, be understood to mean in the following account of its properties and preparation, is a compound of it with water; it is a nitrate of water, or, as it is popularly termed, liquid nitric acid, or aquafortis.

To prepare liquid nitric acid from nitrate of potash, equal weights of this salt and of oil of vitriol are mixed in a glass retort, A, which is placed in a furnace, supported in a sand bath, as in the figure. The oil of vitriol consists of sulphuric acid and water, and by the reaction which ensues, the sulphuric acid combines with the potash of the nitre, while the water of the oil of vitriol uniting with the nitric acid, forms the liquid nitric acid, which distils over, and is condensed in the receiver, B. To render the condensation more complete, this is surrounded by a net, and placed in a trough, *c c*; a stream of cold water flows continually on it from the pipe *i*, and being distributed evenly over the surface by the network, flows out by the exit pipe of the trough, *l*, and escapes into *d e*. Using the proportions just noticed (equal weights), the quantity of sulphuric acid present is double that necessary to neutralize the potash of the nitre, and completely expel the nitric acid; for



The nitre consists of		Oil of vitriol consists of	
One atom nitric acid,	54·0	One atom sulph. acid,	40·1
One atom potash .	47·3	One atom water .	9·0
	101·3		49·1

These, reacting upon each other, should produce,

Sulphate of potash consisting of		Liquid nitric acid formed of	
One atom sulph. acid,	40·1	One atom nitric acid,	54·0
One atom potash .	47·3	One atom water .	9·0
	87·4		63·0

And hence nitre might be decomposed by half its weight of oil of vitriol; but the following reasons prevent those proportions being employed in practice.

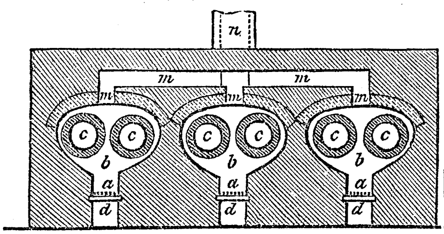
When oil of vitriol acts upon nitre, there is at first but one half of the sulphuric acid taken by the potash, and the sulphate of potash so produced unites with the remaining oil of vitriol (sulphate of water) to form bisulphate of potash, thus, $2(S.O_3 . H.O.)$ and $K.O. N.O_5$ give

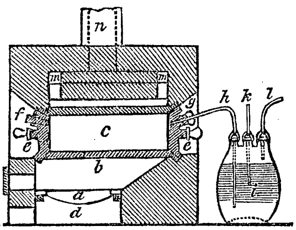
$$(S.O_3 . H.O.+K.O. . S.O_3) \text{ and } H.O.\ N.O_5.$$

If there be oil of vitriol enough, the nitre is thus perfectly decom-

posed at a temperature not exceeding 260° F., and the bisulphate of potash which remains is very easily soluble and fusible, and may hence be removed from the retort without inconvenience. But if the nitre and oil of vitriol be used in the proportion of an equivalent of each, or by weight in round numbers of two parts of nitre to one of oil of vitriol, then one half of the nitre remains at first totally unacted on, and the retort contains, when the process is half finished, a pasty mass of bisulphate of potash and of nitre, which do not fully act on each other until the temperature rises to 400°. The nitre is then decomposed; the nitric acid distils over, and there remains in the retort a mass of neutral sulphate of potash, which can seldom be removed from glass vessels with success. The high temperature necessary also increases very much the risk of the apparatus breaking.

The scientific chemist and the apothecary, however, do not prepare nitric acid; it is made on the large scale for the purposes of the arts, and the processes of purifying the acid of commerce is so simple that no other source is required. On the great scale the nitric acid is prepared, not in glass retorts, but in iron cylinders, connected with condensers, as represented in the figures, one being a section perpendicular to the axes of the cylinders, and the other a section parallel to the axes: the same letters apply to both.





a is the grate, and *d* the ashpit of the furnace, *b*. In each furnace two cast iron cylinders, *c*, *c*, are set, of such capacity that about 1½ cwt. of the nitrate used may be decomposed at once. The ends of the cylinders are closed by covers, *e*, *e*, in one of which is fixed a tube, *f*, for introducing the oil of vitriol, and to the other is adapted a tube of glazed earthenware, *g*, *h*, by which the vapours of the nitric acid are conducted to the range of condensing jars of earthenware, fitted with safety tubes, of which the first is seen in the figure, as *h*, *l*, *k*. The flues, *m*, *m*, *m*, pass from the furnaces to the chimney, *n*. As in this apparatus the temperature can be raised to dull redness without injury, and as the residuum can be removed in the solid form, a smaller quantity of oil of vitriol may suffice, and is generally used.

Since the introduction of nitrate of soda into commerce, it has almost completely superseded nitrate of potash for making nitric acid. It is much cheaper, and it yields a larger product. It does not require, either, so much sulphuric acid nor so high a temperature. The nitrate of soda consists of

One equivalent of nitric acid	54·0
One equivalent of soda	31·3
	85·3

and hence 100 parts of it yield about 74 parts of liquid nitric acid, while 100 parts of nitrate of potash yield but 62.

In making nitric acid, there always occurs at the commencement of the process a disengagement of red fumes, which dissolve in the liquid acid which comes next, and tinge it yellow. This arises from the oil of vitriol in excess abstracting the water from some of the nitric acid, which then is decomposed into nitrous acid, and some oxygen becomes free. At the termination of the process, if the tem-

perature pass much beyond 300°, there is a new evolution of red fumes, for the nitric acid is then similarly decomposed into $N.O_4$ and O.

The strongest nitric acid that can be thus made is of specific gravity 1·521, and consists of $N.O_5 + H.O$.

One equivalent of nitric acid . . .	54·0	or per cent.	85·71
One equivalent of water	9·0	"	14·29
	63·0		100·00

It boils at 187° F., but cannot be distilled without partial decomposition. The acid is very seldom obtained of this strength. In general, the specific gravity of the strong liquid acid is 1·500, and it consists of $2N.O_5 + 3H.O$.

Two equivalents of nitric acid . .	108·0	or per cent.	80·00
Three equivalents of water . . .	27·0	"	20·00
	135·0		100·00

When the nitric acid is gradually mixed with water, the boiling point rises until when the specific gravity is 1·420, it boils at 248°. If it be farther diluted, the boiling point is again lowered. At this point the acid has a definite chemical constitution; it consists of $N.O_5 + 4H\,O$.

One equivalent of nitric acid . . .	54·0	or per cent.	60·22
Four equivalents of water	36·0	"	39·78
	90·0		100·00

The liquid nitric acid is, when pure, completely colourless; it fumes when exposed to the air, and if exposed to the direct solar light, very soon becomes deep yellow, while oxygen gas is disengaged; the same decomposition into nitrous acid and oxygen gas may be instantly effected by passing the vapours of the acid through a red-hot porcelain tube. In a great variety of processes where substances are to be oxidized, nitric acid is employed. It acts with remarkable rapidity on the generality of the metals and of organic bodies, supplying oxygen for the constitution of a variety of new compounds, and being itself reduced to the state of nitric or nitrous oxide, or even pure nitrogen.

If the organic body do not contain nitrogen, it is generally ultimately converted into the oxalic and carbonic acids; with animal substances, new bodies are formed of a deep yellow colour, and hence the stains produced upon the nails and fingers where nitric acid touches, and it is hence used for stamping the yellow patterns on woollen table covers. The decomposition of the acid is generally accompanied by the production of red fumes.

In its action on the metals, nitric acid presents some remarkable anomalies; when of the specific gravity of 1·48, it may be put into contact with tin or iron without acting on those metals, although, if a little stronger or weaker, its action is very great; and this inactive acid may be brought into activity by various means, as by touching the immersed metal with another different one. These phenomena appear to involve conditions probably electrical, which are not, as yet, completely understood.

The nitric acid prepared by decomposing nitre by half its weight of oil of vitriol, is always of a deep red or orange colour, owing to a quantity of the acid having been decomposed into nitrous acid, which remains dissolved. This deep-coloured acid is frequently

useful, as it gives off oxygen still more easily than the pure acid, and is hence sometimes applicable as an oxidixing agent where the colourless acid fails. A deep red fuming acid may be prepared by passing a stream of nitric oxide gas through the colourless acid; it is absorbed in great quantity, and the liquor assumes successively various shades of yellow, green, and red, according to its state of dilution. The nitric oxide ($N.O_2$) decomposes the nitric acid ($N.O_5$), and forms nitrous acid ($N.O_4$), which dissolves in the excess of liquid acid. If it be required to obtain a colourless acid, it is sufficient that the coloured acid should be boiled for a few minutes; all the nitrous acid fumes pass off, and the nitric acid remains colourless, though somewhat weaker.

I have mentioned that the nitric acid is not prepared on the small scale, as the commercial aquafortis is easily purified. The impurities of it are, generally, chlorine, arising from the nitre employed having contained common salt; sulphuric acid, from some having been distilled over by too great heat; and some iron, arising from the cylinders or stoneware bottles in which the acid is preserved. These may be easily detected; on mixing a few drops of the commercial acid with half an ounce of distilled water, a drop of solution of nitrate of barytes will give a precipitate if sulphuric acid be present; nitrate of silver will indicate, by a precipitate, the presence of chlorine; while a little solution of yellow prussiate of potash will form Prussian blue if the acid contained any iron. From these impurities the acid may be freed by being redistilled; the chlorine passes off along with the portions which first come over, and by thus testing from time to time the acid which is thus obtained, it will be found no longer to precipitate the nitrate of silver, and may then be considered pure; the iron and sulphuric acid remain behind in the retort, provided the distillation be not pushed too far. I have found that from twelve pounds of commercial aquafortis there can be obtained eight quite pure, three being allowed to come over first to carry off the chlorine, and one being left in the retort with the fixed impurities.

The detection of nitric acid is not difficult; it cannot be recognised by forming precipitates, as all its neutral salts are soluble, but its properties are very marked. 1st, The production of red fumes by nitric oxide when it is brought into contact with a metal, is characteristic of it. 2d, When a drop of nitric acid is added to water tinged blue by sulphate of indigo, and the mixture boiled, it is bleached by the oxidizement of the indigo by the acid. 3d, When a small crystal of protosulphate of iron is placed in contact with water containing nitric acid, a ring of deep olive-coloured liquid forms round it, according as it dissolves; from one portion of the protosulphate reducing the acid to the state of nitric oxide, which then combines with the remaining protosulphate. 4th, Nitric acid confers upon muriatic acid the power of dissolving gold leaf, but this test is not of such distinctness as the others, from the same effect being produced by the chloric and some other acids. 5th, Nitric acid may also be distinguished by the deep red colour it produces with a crystal of morphia.

For the detection of a small quantity of nitric acid, the best plan

is to neutralize the liquor, if it be acid, by a solution of potash, and to evaporate to dryness. The salt so obtained crystallizes in sharp needles, and deflagrates when placed on ignited charcoal; heated with a little bisulphate of potash and some copper filings, it evolves copious red fumes, and with a drop of sulphuric acid and a crystal of protosulphate of iron, produces the olive-coloured liquor already noticed. All solid compounds of nitric acid, such as the basic nitrates, may be recognised in this way.

The nitric acid not being isolable, we do not know the state of condensation of its elements, which are united in the proportion of two volumes of nitrogen to five of oxygen. Its composition by weight and its equivalent numbers are as follows:

Nitrogen,	26·15	One equivalent,	=175	or 14·0
Oxygen,	73·85	Five equivalents,	=500	or 40 0
	100·00		675	54·0

The specific gravity of the vapour of the liquid nitric acid, $H.O..N.O_5$, is not known; but Bineau has found the sp. gr. of the vapour of the liquid acid, which boils at 248°, $H.O..N.O_5+3H.O.$, to be 1243, which might result from

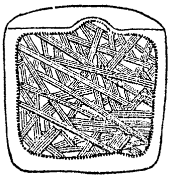
Two volumes of nitrogen	976×2=1952·0
Five volumes of oxygen	1102·6×5=5513·0
Eight volumes of watery vapour	620·1×8=4960·8
condensed into ten volumes	12425·8
of which one, therefore, should weigh	1242·6

This result requires confirmation.

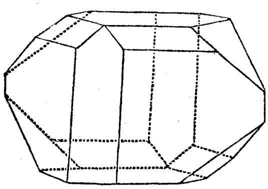
Sulphur.

This substance exists in large quantity in nature in combination The most important ores of copper, lead, silver, mercury, antimony, and many other metals, are their sulphurets; and a great quantity of the sulphur at present used in commerce is derived from the iron pyrites, bisulphuret of iron. Sulphur is exhaled in large quantity also from volcanoes, partly uncombined, partly in the state of sulphuret of hydrogen, arising probably from the decomposition of metallic sulphurets by the high temperature in the interior of the earth. The native sulphur so produced, condensing in fissures, constitutes the great deposites of volcanic sulphur of Sicily and other places, which supply a large proportion of that employed in commerce. It exists also native, combined with oxygen and various metallic oxides, forming native sulphates, of which those of lime and of barytes are the most abundant. In many organic bodies, also, sulphur exists as a constituent, as in the white, and particularly the yolk of egg, the hair, the horns, and hoofs of animals, and in the black mustard-seed it exists in considerable quantity.

At ordinary temperatures sulphur exists generally as an opaque solid, sp. gr. 1·98. When heated, it melts at 226° into an amber-coloured thin liquid; if the temperature be then raised to about 400°, it becomes dark brown, opaque, and so thick that the vessel containing it may be inverted without its pouring out; but when heated farther it becomes thinner, until at 601°, its boiling point, it is as thin and limpid as when first it began to melt. If the sulphur, when just melted, be allowed to cool slowly, and the internal liquid be



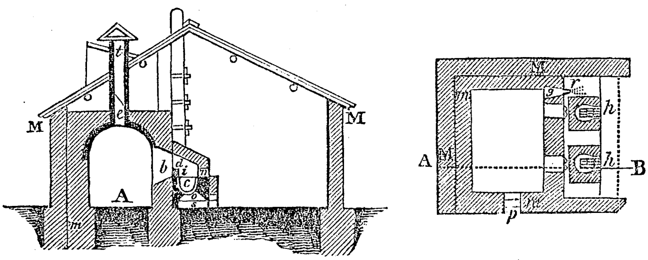
poured out when the outer crust has solidified, the interior will be found lined with crystals, as in the figure, which have the form of the oblique rhombic prism, of which a common modification with secondary faces, and the surfaces of the octohedron, which determines the height of the principal axis of the crystal, is given. These crystals, when first obtained, are transparent and amber-coloured, but after a few days they become opaque, sulphur yellow, and friable, being then changed into the dimorphous state.



If the thick tenacious sulphur at 400° be suddenly cooled by immersion in a large quantity of water, it forms a soft and transparent mass of considerable elasticity, and may be drawn out into long threads like India rubber; after some time, however, it changes into the ordinary state.

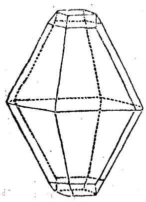
Sulphur is used in pharmacy under two forms, that of roll and flowers; the former is made by melting the rough native sulphur, and pouring it into slightly conical moulds, in which it solidifies. The flowers of sulphur are formed by the condensation of the vapour of sulphur so rapidly that the molecules have not time to form crystals of any perceptible size, so that the condensed sulphur, although really crystalline, appears to the sight and touch as an impalpable soft powder.

For the manufacture of flowers of sulphur, the apparatus is arranged as in the subjoined figures, in which A is a vertical and B a horizontal section, to which



the same letters refer. In an apartment and shed, M, M, a chamber, A, is constructed, which must have at least 2000 cubic feet capacity. Outside of this chamber is an iron pan, *c*, in which, by a fire at *o*, the sulphur is kept gently boiling. The boiler and fireplace must be completely surrounded by brickwork, so that as little heat as possible may be communicated to the vaulted chamber, A; the draught from the fire passes to the chimney, *g*; the pan is supplied with sulphur by the door, *n*, which can be closed air-tight; the vapour of sulphur mixes with the air in the wide space, *d*, over the boiler, and, passing through the aperture *b*, rises into the chamber, where, mixing with the large mass of cold air, the sulphur is condensed, and falls like a fine snow shower upon the floor underneath. When a sufficient quantity of the flowers of sulphur have been thus formed, they are removed by the door at *p*. If, at the commencement of the process, the mixture of sulphur-vapour and air should inflame, the explosion opens the valve at *e*, the gases escape at *t*, and all danger is avoided.

The form of crystal of sublimed sulphur is the right rhombic octohedron, of which a common modification is represented in the



margin. Sulphur is found crystallized in this form on the edges of the craters of most volcanoes, the crystals being transparent, and sometimes of considerable size. When sulphur is deposited from its solution in chloride of sulphur or in sulphuret of carbon, it is in this form also that its particles arrange themselves.

Sulphur may be obtained, however, in a state of much more minute division, and destitute of all crystalline structure, by precipitation from solution. Thus, if the persulphuret of potassium, $K.S_5$, be decomposed by muriatic acid, four equivalents of sulphur are set free, and separate as a milk-white powder. This constitutes the *Sulphur Precipitatum* of pharmacy. In all cases where sulphur is precipitated from a cold solution, it is pure white.

Sulphur is not soluble in water or in alcohol; it dissolves in the oils, still more in those liquids mentioned above. It dissolves in alkaline solutions, or in milk of lime; but there then occur complex reactions, which will be studied hereafter.

When sulphur is boiled it forms a deep yellow vapour, the specific gravity of which is 6648. Sulphur evaporates, however, very rapidly long before it boils, and even forms some vapour below its melting point. At a temperature of about 300° it takes fire, burning with a bluish violet flame, and forming sulphurous acid ($S.O_2$).

The resemblance of sulphur to oxygen in its chemical relations is very striking, by combining with the same bodies, according to the same proportions, they generate completely parallel classes of acids, bases, and salts. Thus, with carbon and potassium, there are formed

$C.O_2$ Carbonic acid.	$C.S_2$ Sulpho-carbonic acid.
$K.O.$ Oxide of potassium.	$K.S.$ Sulphuret of potassium.
$\overline{K.O.\,.\,C.O_2}$ Carbonate of potassium.	$\overline{K.S.\,.\,C.S_2}$ Sulpho-carbonate of potassium.

and with arsenic and potassium,

$As.O_5$ Arsenic acid.	$As.S_5$ Sulpharsenic acid.
$K.O.$ Oxide of potassium.	$K.S.$ Sulphuret of potassium.
$\overline{K.O.\,.\,As.O_5}$ Arseniate of potassium.	$\overline{K.S.\,.\,As.S_5}$ Sulpharseniate of potassium.

In like manner, the similar compounds Fe_3O_4 and Fe_3S_4 are not altered by heat, but are magnetic, while $Fe.S_2$ and $Mn.O_2$ give out oxygen and sulphur, and are reduced to Fe_3S_4 and Mn_3O_4. I shall have frequent occasion to revert to these considerations, which have already been noticed under another point of view (p. 238).

The equivalent number of sulphur is 16·1 or 201·2, and its combining volume one third that of oxygen.

Sulphur combines with oxygen, forming

Sulphurous acid	$S.O_2$.
Sulphuric acid	$S.O_3$, or $S.O_2\,.\,O$.
Hyposulphurous acid	S_2O_2, or $S.O_2\,.\,S$.
Hyposulphuric acid	S_2O_5, or $2S.O_2\,.\,O$.

Sulphurous Acid.

Sulphurous acid exists at ordinary temperature and pressure in the gaseous form; it is one, however, of the most easily liquefied gases. It is produced always when sulphur burns either in air or in pure oxygen, sulphur not being capable of passing directly to a

higher degree of oxidation. In the burning of sulphur, the volume of sulphurous acid gas formed is exactly equal to that of the oxygen consumed.

When required pure, it is prepared generally by decomposing sulphuric acid by means of a metal not very easily oxidized, as mercury or copper. The metal combines with one atom of the oxygen of the sulphuric acid, and the sulphur, with the remaining two atoms of oxygen, pass off as sulphurous acid gas; the oxide formed unites with the remaining sulphuric acid to form a salt. Thus, if mercury be used, $S.O_3$ and Hg. give $S.O_2$ and Hg.O., and Hg.O. unites with $S.O_3$ to form sulphate of mercury. If the heat be not raised beyond 200° in this process, it is black oxide of mercury which is produced ($Hg_2O.$), but above that degree the red oxide (Hg.O.) alone is formed.

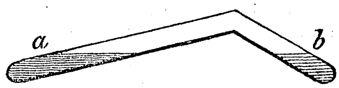
Sulphurous acid gas may also be very simply prepared by heating three parts of flowers of sulphur with four of peroxide of manganese. The reaction is very simple; one part of the sulphur uniting with the metal, and another with the oxygen, form sulphuret of manganese and sulphurous acid; thus, $Mn.O_2$ and 2S. give Mn.S. and $S.O_2$. The apparatus used in these processes may be that figured under the heads of oxygen (p. 244) or nitrous oxide (p. 272).

Sulphurous acid gas is absorbed by water; and hence, in order to examine its properties in that state, it must be collected over mercury. It is colourless and transparent, possessing an odour peculiarly irritating (the smell of burning sulphur), and cannot be breathed. It is not combustible, nor does it support combustion. It bleaches a variety of vegetable and animal bodies, and is hence used in the arts to whiten straw bonnets, corn, silk, sponges, and other substances. The bleaching is produced by the sulphurous acid combining with the coloured substance, and forming a white compound, from which the gas gradually escapes on exposure to air, and hence such bleaching is not permanent. The sulphurous acid may be expelled, also, from this kind of compound by a stronger acid, and the colour generally restored; thus, if a red rose be exposed to the fumes of burning sulphur, it becomes completely white; but if washed in dilute sulphuric acid, its red colour is perfectly renewed.

The specific gravity of sulphurous acid gas is 2210·6, and it is formed by

One volume of sulphur-vapour	6648·0
Six volumes of oxygen	6615·6
The seven volumes condensed to six, give . .	13263.6
Weight of one volume of $S.O_2$	2210·6

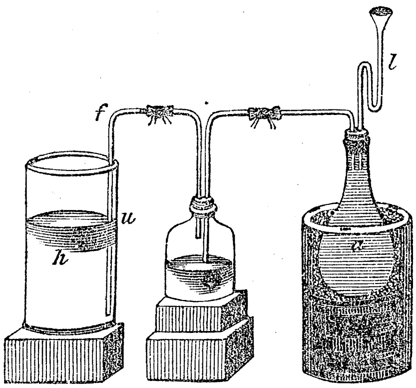
When this gas is exposed to a cold of 0° F., it condenses into liquid heavier than water, which boils at 14°, and produces by its evaporation a very intense cold; it is easily obtained in the liquid form by putting a quantity of mercury and oil of vitriol into a tube, and sealing



up the ends, as in the figure; on applying heat to the extremity *a*,

containing those materials, and cooling the other end by means of ether, the gas evolved is liquefied by its own pressure, and collects in quantity at *b*.

When a large quantity of sulphurous acid is required dissolved in water, or when it is to be employed to form compounds with bases, it may be produced in a much cheaper way than those described above. Into a matrass, *a*, placed in a furnace, is introduced a quantity of well-burned charcoal, in bits about the size of a hazel-nut, and by means of the safety-funnel *l*, as much oil of vitriol is poured in as that the mixture shall half fill the vessel; a tube passes to a bottle, *i*, containing some water to wash the gas from any adhering sulphuric acid, and it is then conducted by the tube *f*, which passes to the bottom of the vessel *h*, containing the liquor in which the gas is to be dissolved. On applying heat, the carbon of the charcoal abstracts from the sulphuric acid one third of its oxygen, so that with C. and $2S.O_3$ there are formed $C.O_2$ and $2S.O_2$; there is produced a mixture of two volumes of sulphurous acid and one of carbonic acid, which last cannot enter into combination, and passes off from the apparatus without change.



Water dissolves about thirty-seven times its volume of sulphurous acid; the solution possesses the properties of the gas in a very high degree, and bleaches vegetable colours with great power; when kept for some time, it gradually absorbs oxygen, and the sulphurous becomes changed into sulphuric acid.

The sulphurous acid is one of the feeblest acids, and is expelled from its combinations by almost all but the carbonic acid. Of its salts, those which are soluble, all possess alkaline reaction.

The sulphurous acid passes into the state of sulphuric acid by absorbing oxygen from many bodies; thus, when it is heated with a solution of gold or silver, or of mercury, these metals are reduced to the metallic state; others yield but a part of their oxygen; thus the peroxide of iron abandons a third, and the black oxide of copper one half of that constituent.

The salts of sulphurous acid possess the same deoxidizing power.

The composition and equivalent of sulphurous acid are as follows:

Sulphur,	50·14	One equivalent,	=201·2 or	16·1
Oxygen,	49·86	Two equivalents,	=200 0 or	16·0
	100·00		401·2	32·1

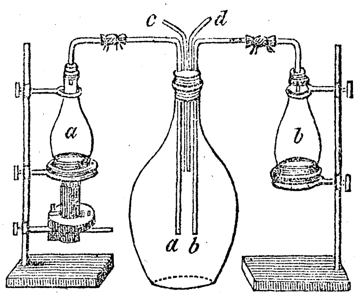
Sulphuric Acid.

$S.O_3$.

Sulphuric acid, one of the most important compound bodies, from the energy of its action, and the variety of combinations which it forms, is not produced by the direct union of oxygen and sulphur in any case, but arises from the combination of sulphurous acid with another quantity of oxygen. Thus, by the action of sulphurous acid on the easily reducible metallic oxides, sulphuric acid is produced. This principle is beautifully shown by passing a mixture of sulphur-

ous acid gas and air through a tube filled with spongy platinum, and heated to dull redness, when there issues from the extremity a mixture of vapour of sulphuric acid, mixed with the residual nitro gen of the air; by such processes, however, it could not be formed in quantities suited to the purposes of commerce.

The preparation of sulphuric acid is effected upon the large scale by bringing sulphurous acid, produced by the burning of sulphur, into contact with watery vapour and nitrous acid fumes; these unite to form a white crystalline solid, which appears to be a compound of sulphurous acid and nitrous acid ($S.O_2+N.O_4$), united with a quantity of sulphuric acid and water which is not constant. The formation of this substance may be shown by the arrangement in the figure. The central vessel, the inner surface of which is slightly moistened, contains atmospheric air; by means of the tubes, sulphurous acid gas generated in the flask *a*, and nitric oxide formed in *b*, are introduced, to the latter of which the oxygen is supplied by the air to form nitrous acid fumes; the interior of the vessel becomes gradually covered with a deposite like hoar-frost, consisting of this substance; and, in order that its production may proceed without interruption, the vessel may be filled with fresh atmospheric air by blowing through one of the tubes *c*, *d*, while the residual gases are expelled through the other.



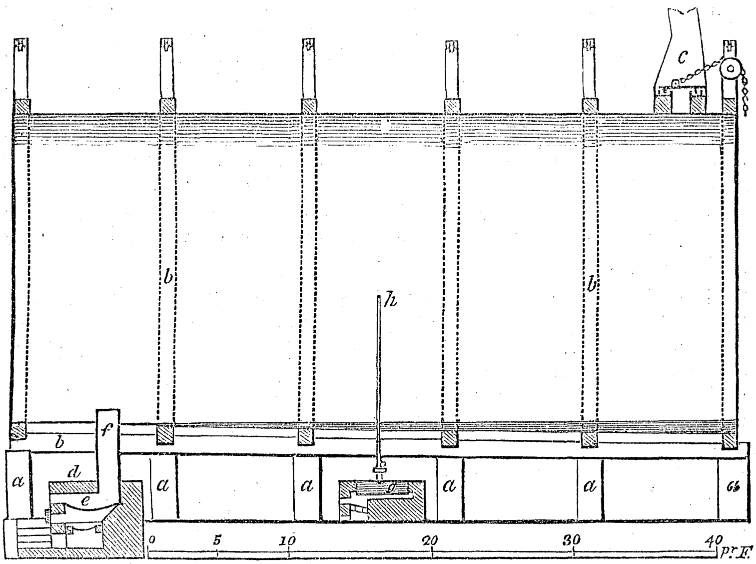
This crystalline substance is decomposed by a larger quantity of water; hence, if the bottom of the central vessel be covered by a layer of water, the crystalline substance falling into it according as it is generated, is resolved into sulphuric and hyponitric acids; thus $S.O_2+N.O_4$ gives $S.O_3$ and $N.O_3$, which last is decomposed by the water into nitric acid and nitric oxide, $3N.O_3$ giving $N.O_5$ and $2 N.O_2$; the nitric acid remains combined with the water along with the sulphuric acid, while the nitric oxide escaping with effervescence, generates, on arriving at the air, a new quantity of red fumes, and oxidizes a new quantity of sulphurous acid.

It was supposed that a certain quantity of water was necessary to the existence of this solid body, although a larger quantity decomposed it; but it has been found that a similar substance may be formed which contains no water. Sulphurous and nitrous acids do not act on each other when in the gaseous form, unless water be present; but they combine if placed in contact under considerable pressure, and liquid, even when completely dry. A portion of the nitrous acid converts an equivalent of the sulphurous acid into sulphuric acid, it being itself reduced to the state of hyponitrous acid, while another quantity of nitrous and sulphurous acid unites directly; there are thus formed from $2S.O_2$ and $2N.O_4$ a white crystalline solid $S.O_2 . N.O_4+S.O_3$, and a quantity of $N.O_3$, which is given off on the tube in which the combination is produced being opened.

It may be questioned, however, whether this substance, for the discovery and analysis of which we are indebted to M. de Prevostaye, interferes in the formation of sulphuric acid on the large scale, where the nitrous and sulphurous acids act on one another in the gaseous forms.

In the manufacture of sulphuric acid, the apparatus consists of a long leaden chamber consisting of two portions; the lower a tray of about $1\frac{1}{2}$ feet deep, the

other a quadrangular bell, which, being suspended on a wooden framework, *b*, *b*, rests with its edges immersed in the liquid, with which the tray is filled, like the cylinder of a bell gasometer. The bottom of the chamber, which is supported at a certain distance from the ground on pillars, *a*, *a*, *a*, slants from before, so that the



liquid which occupies it increases in depth towards the end. Under the front is placed a furnace, *d*, on the floor of which, *e*, the sulphur is burned, and the sulphur ous acid passes into the chamber by the chimney *f*; the heat necessary is supplied by the fireplace under *e*; the nitrous acid is obtained by placing over the burning sulphur in *e* a pan containing a quantity of nitrate of soda and oil of vitriol, the nitric acid evolved from which directly oxidizes a portion of sulphurous acid, and then, being brought to the state of $N.O_4$, acts on the mass of sulphurous acid as has been just described: *g* is a boiler, by which steam is driven into the chamber at *h*, and thus, in the interior, are provided the conditions for the reunion of steam, sulphurous acid gas and nitrous acid fumes, which produce, as in the apparatus figured already, the white crystalline solid, by which, when decomposed by the water at the bottom of the chamber, the sulphurous acid is produced, and nitric oxide gas evolved. This nitric oxide, mixing with the atmospheric air, which is always present in large excess in the interior of the chamber, is reconverted into nitrous acid, which combines with a new quantity of sulphurous acid, generating another proportion of the solid body, from whose decomposition by the water the nitric oxide is again evolved with little loss; and thus the oxygen of the air is gradually transferred to the sulphurous acid by the intermediate agency of the nitrous acid fumes. Were there no nitric acid formed, the same quantity of nitric oxide might convert an infinite quantity of sulphurous acid into sulphuric acid; but as the oil of vitriol produced always retains a certain proportion of the nitric acid, it is necessary to supply its loss, and to send into the chamber a continued current of nitrous acid fumes. This is secured by the construction already described, about one part of nitrate of soda being decomposed for every eight or nine parts of sulphur burned in the furnace *d*, *e*. The draught is regulated by the chimney *c*, which is fitted with a valve, by the position of which a current of air is established through the chamber sufficient to bring the gases into complete mixture inside, and in due proportions, but which does not carry them away until their action is completed.

The inclination given to the bottom of the chamber is for the purpose of allowing the water, which, having dissolved most of the sulphuric acid, and become heavy, to flow down to the farthest end; and thus there is, on the surface has next the front, a layer of the weakest acid, ready to absorb and decompose the great

quantity of the crystalline body formed when the mixed sulphurous and nitrous acid gases meet the damp atmosphere of the chamber.

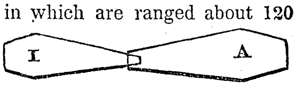
The water in the chamber is allowed to remain unchanged until it has attained a specific gravity of about 1·600; it is then removed by leaden pipes, and concentrated by evaporation in leaden cisterns, until its specific gravity is increased to about 1·76. At this strength it begins to act upon the lead, and must be transferred to vessels of glass, or, still better, of platinum, in which the concentration may be finished. In the strongest form in which it can be so obtained, its specific gravity is 1·847, and it contains 81·54 of real acid in 100.

Thus is the oil of vitriol of commerce manufactured. At present, a modification of the process has been introduced, in consequence of the extensive use of the iron pyrites (bisulphuret of iron, $Fe.S_2$) in place of sulphur, as the source of the sulphurous acid. Instead of the furnace *e*, *f*, there is built in front of the chamber a kiln, somewhat like a limekiln, except that it is narrowed at top into a chimney passing into the chamber. At the bottom of the kiln is placed a layer of coal or wood, on it the pyrites in small pieces. The fire is lighted, and the ignition being communicated to the pyrites, the sulphur burns, forming sulphurous acid, which is conducted into the chamber, while the iron remains behind as peroxide. The pan with nitre and oil of vitriol is supported in the kiln at such a height above the mass of burning pyrites as that the temperature may not be too great. As the combustion proceeds, new quantities of pyrites are introduced by apertures high up in the kiln, while the residue of adherent rock and oxide of iron is raked out from the ashpits at the bottom.

A form of sulphuric acid is prepared upon the Continent, and known as German oil of vitriol, or fuming sulphuric acid, which is much stronger than can be made by the combustion of sulphur, as has been described.

It is obtained by exposing sulphate of iron to a red heat, in earthen retorts. If the sulphate of iron, perfectly dry, be strongly heated, the sulphuric acid is driven off, and oxide of iron remains behind; but the acid is mostly resolved into sulphurous acid and oxygen, and consequently lost. But if the sulphate of iron be not completely dried, the sulphuric acid combines with the water, and, distilling over in combination with it, forms a dark-coloured liquid of a thick, oily consistence, specific gravity about 1·9, and consisting generally of about 90 of real acid and 10 of water in 100, approaching closely to the formula $2S.O_3+H.O.$ At the same time, a quantity (one half) of the acid is decomposed, the iron becoming peroxidized, and sulphurous acid gas being evolved. Thus $4(S.O_3+Fe.O.)$ and $H.O.$ give $2S.O_3+H.O.$ and $2S.O_2$, leaving behind $2Fe_2O_3$, known in commerce as colcothar of vitriol.

This process is carried on in a long furnace, in which are ranged about 120 earthen retorts, as I, in rows of 20, containing the partially-dried sulphate of iron. They are gradually heated until the fumes of sulphuric acid begin to appear, and the receiver A is then attached, in which the acid is condensed by means of cold applied externally.



When this fuming sulphuric acid is heated, it is resolved into ordinary oil of vitriol and real sulphuric acid. This last, being very volatile, distils over in colourless vapours, which, on coming into contact with moist air, form dense white fumes of liquid acid. If the colourless vapour be received in a dry vessel, cooled by a freezing mixture, it condenses in beautiful white satiny fibres, constituting the dry sulphuric acid. This acid melts at 77°, and very little above that temperature it boils. The specific gravity of its vapour is 2762, formed by

One volume of vapour of sulphur		= 6648·0
Nine volumes of oxygen	1102·6×9	= 9923·4
The ten volumes forming six		=16571·4
Of which one weighs, therefore		2761·9

When this dry sulphuric acid in vapour is brought into contact

with dry barytes, lime, or magnesia, they combine with brilliant combustion, forming sulphates of those earths. When a mass of the crystals is thrown into water, it hisses as on the immersion of red-hot iron, and ordinary liquid sulphuric acid is produced.

There exist several definite compounds of sulphuric acid with water, of which the most remarkable are two: the first is the strongest oil of vitriol made in this country, and contains an equivalent of acid united to one of water; its formula is $S.O_3 + H.O.$; its most important properties have been already described. The other contains twice as much water; its formula being $S.O_3 + 2H.O.$; its specific gravity is 1780. When exposed to the temperature of melting ice, this acid forms large and regular crystals, while the stronger or weaker acids require very intense cold to solidify them. When oil of vitriol is mixed with water, the great heat which is produced results from the formation of definite compounds; and it has been already shown (page 185) that, no matter what combination a certain quantity of sulphuric acid forms, it evolves the same quantity of heat on entering into union.

Sulphuric acid, formed by the combustion of sulphur, as described, in leaden chambers, is liable to be contaminated by the presence of some nitric acid and lead; from these it may freed by redistillation, which should, however, be conducted with great care, as the vapour of the acid forms interruptedly and by sudden bursts, which might endanger the apparatus. On diluting common oil of vitriol, a white powder is generally seen to form, which is sulphate of lead, that had been held in solution by the strong acid, but which precipitates from the diluted acid. The acid now formed from the iron pyrites is found to contain frequently arsenic and selenium: the presence of the former may become of great importance in medico-legal investigations, and the detection of it will be fully described in its proper place.

Sulphuric acid is very easily detected by means of a solution of nitrate of barytes. If the smallest quantity of sulphuric acid be present, a white precipitate is formed, which is insoluble in muriatic acid, even when boiled.

Sulphuric acid appears to dissolve certain bodies in small quantity, which are not soluble without alteration in any other medium. These are sulphur, carbon, tellurium, and selenium. These solutions are not, however, of any independent interest.

Hyposulphurous Acid.

S_2O_2, or $S.O_2 + S.$

When a stream of sulphurous acid gas ($S.O_2$) is passed into a solution of sulphuret of calcium, it is absorbed, a quantity of sulphur is precipitated, and the liquor, when filtered, is found to be a solution of hyposulphite of lime. The reaction which occurs is simple. Half of the oxygen of the sulphurous acid passes to the calcium to form lime, reducing the sulphurous to the state of hyposulphurous acid, and, at the same time, the sulphur which had been combined with the calcium is set free, $2Ca.S.$ and $2S.O_2$ giving $2Ca.O. + S_2O_2$, while $2S.$ is precipitated.

This acid is also formed when sulphur is boiled with an alkaline liquor or with milk of lime. Thus, when soda and sulphur are boiled in water, the liquor contains hyposulphite of soda and sulphuret of sodium, produced by $3Na.O.$ and $4S.$ giving $Na.O. + S_2O_2$ and $2Na.S.$

This acid itself is very easily decomposed; it may, however, be obtained, at

least for a time, in a free state, by adding to any of its salts a stronger acid, or, better, by bringing sulphurous acid and sulphuretted hydrogen gas to meet in water; the reaction which occurs is that $4S.O_2$ and $2S.H.$ give $3S_2O_2$ and $2O.H.$ The water gradually becomes intensely sour, but after some time this acid resolves itself into sulphur and sulphurous acid.

The most remarkable character which the compounds of hyposulphurous acid possess is, that they dissolve those compounds of silver which are insoluble in water, as the chloride and iodide, and form a solution possessing an intensely sweet taste; upon this property is founded their use in Daguerreotype and photogenic drawing. This acid is also recognised by its silver salt being decomposed, when boiled, into black sulphuret of silver and free sulphuric acid, $S_2O_2+Ag.O.$ giving $S.O_3$ and $Ag.S.$ It is an important fact, also, in the history of the hyposulphuric acid, that its salts do not always contain metallic oxides, but that it may form salts with metallic sulphurets; thus there are two hyposulphites of sodium, of which one contains oxide of sodium (soda), the other sulphuret of sodium. Their formulæ are $S_2O_2+Na.O.$, and $S_2O_2+Na.S$ Each of these, in crystallizing, combines with ten atoms of water, like common sulphate of soda; they possess, like it, a point of maximum solubility, and the crystals of all three appear to be isomorphous. There are, therefore, three salts,

$$S.O_2\ .\ S.+Na.S.+10H.O.,$$
$$S.O_2\ .\ S.+Na.O.+10H.O.,$$
$$S.O_2\ .\ O.+Na.O.+10H.O.,$$

the similar constitution of which evidences the relation of sulphur and oxygen in a remarkable degree, and will furnish the ground of speculations of great interest, to which I shall again recur.

Hyposulphuric Acid.

$$S_2O_5, \text{ or } S_2O_4+O.$$

When sulphurous acid gas is passed through water in which pure peroxide of manganese is diffused, this dissolves, and the solution contains neutral hyposulphate of manganese. The reaction by which it is produced is simply that the second atom of oxygen of the peroxide of manganese converts two equivalents of sulphurous acid into hyposulphuric acid, which is exactly neutralized by the protoxide of manganese that is evolved, $Mn.O_2$ and $2S.O_2$ giving $Mn.O.+S_2O_5$.

When a salt of hyposulphuric acid is heated, it is resolved into sulphurous acid, which passes off as gas, and a neutral sulphate which remains behind, $S_2O_5+R.O.$ giving $S.O_2$ and $S.O_3+R.O.$ The acid may be obtained free by decomposing its barytes salt by sulphuric acid, but it cannot be kept long. When heated, it gives off sulphurous acid, and sulphuric acid remains; and even when cold it rapidly forms sulphuric acid by absorbing oxygen.

Remarks on the Constitution of the Compounds of Oxygen and Sulphur.

The progress of science has gradually brought into view a number of facts, by which it is now very nearly fully established, that of the bodies just now described, we must look upon the sulphurous acid as the only direct compound of sulphur and oxygen, and that in the others, sulphurous acid must be considered as pre-existing. The reasons for this are very numerous. By the direct union of sulphur and oxygen we can never obtain any other compound than sulphurous acid; the others being always formed from it, prepared either perfectly distinctly, or at the moment of the reaction, and then presented to other elements with which it may unite.

On this view the necessity of the indirect process of manufacture of sulphuric acid becomes evident. The sulphur, when it forms sulphurous acid, is fully saturated with oxygen, and cannot combine with any more; but the sulphurous acid ($S.O_2$) acts as a compound radical, like cyanogen, as described in p. 233, and may unite with

any of the simple and compound bodies. It does not unite directly with oxygen, but it does so with nitrous acid, and the body so formed is decomposed by water, producing sulphuric acid, as has been fully described. In like manner, to form hyposulphurous acid, the radical, sulphurous acid, combines with sulphur; the compound is a sulphur acid, $S.O_2+S.$, and combines with sulphur bases to form a distinct class of salts. The hyposulphuric acid contains also sulphurous acid as its basis; but there are two equivalents of the radical to one of oxygen: it is $2S.O_2+O.$ This hypothesis is rendered still stronger by the fact that sulphurous acid combines with chlorine and with iodine to form the chloro-sulphurous acid $S.O_2+Cl.$, and the iodo-sulphurous acid $S.O_2+I.$ It combines also with nitric oxide to form the nitro-sulphurous acid $S.O_2+N.O_2$. The chloro-sulphurous acid is produced by the direct combination of chlorine and sulphurous acid, when exposed to strong sunlight. The iodo-sulphurous acid is formed by passing sulphurous acid gas through a solution of iodine in pyroxylic spirit, and the nitro-sulphuric acid, which exists only combined with bases, by placing a solution of sulphite of potash in contact with nitric oxide, which it gradually absorbs. The sulphurous acid forms, therefore, an extensive range of combinations, in which it serves as a compound radical, and of which the formulæ are as follows:

Sulphuric acid	$S.O_2+O.$
Hyposulphuric acid	$2S\ O_2+O.$
Hyposulphurous acid	$S.O_2+S.$
Chloro-sulphurous acid	$S.O_2+Cl.$
Iodo-sulphurous acid	$S.O_2+I.$
Nitro-sulphurous acid	$S.O_2+N.O_2.$

The ordinary salts of sulphurous acid, the *Sulphites*, I rank along with the compounds of chlorine with the metallic oxides and with peroxide of hydrogen, which bodies they resemble also in their bleaching powers.

Compounds of Sulphur and Hydrogen.

Sulphur unites with hydrogen in two proportions, forming a gas, *Sulphuretted Hydrogen*, by an equivalent of each element, and a heavy liquid when in the proportion of one equivalent of hydrogen to two of sulphur.

To prepare sulphuretted hydrogen, the protosulphuret of iron ($Fe.S.$) is acted on by dilute sulphuric acid, in the apparatus figured in p. 247. A lively effervescence occurs from the escape of sulphuretted hydrogen gas, and the solution contains sulphate of protoxide of iron; a gentle heat may be applied to favour the reaction of the materials. In this process water is decomposed, its oxygen being transferred to the iron, and its hydrogen to the sulphur; the result may be expressed as follows: $Fe.S.$ and $S.O_3+H.O.$ give $H.S.$ and $S.O_3+Fe.O.$ This gas may also be obtained by acting on sulphuret of potassium by dilute sulphuric or muriatic acid, in which case the theory is the same as that already given. Sulphuret of antimony and liquid muriatic acid produce, when heated, very pure sulphuretted hydrogen, the reaction being that Sb_2S_3 and $3(H.Cl.)$ give Sb_2Cl_3 and $3(H.S.)$.

The sulphuretted hydrogen gas, being absorbed by water, cannot be well collected over it, except it be saturated with common salt, or be heated to above 90°, in which case its solvent power is very much diminished. It cannot be kept long over the mercurial pneumatic trough, for the lead and tin always present in the mercury of commerce gradually decompose it, combining with the sulphur, and leaving the hydrogen free; the volume of the gas remains the same during this decomposition.

This gas is colourless and transparent: it is characterized by its fetid odour, that of rotten eggs, which, indeed, owe their peculiar odour to the formation of this gas during their putrefaction. Its specific gravity is 1177. It consists, therefore, of

One volume of vapour of sulphur		6648·0
Six volumes of hydrogen	$68·8 \times 6 =$	412·8
the seven volumes are condensed to six		7060·8
of which one weighs, therefore		1176·8

The sulphuretted hydrogen gas dissolves in water, forming a solution which is extensively used as a reagent for the metals, from the solutions of most of which it precipitates metallic sulphurets of various colours, by which many metals may be recognised. Thus antimony gives an orange, manganese a flesh red, arsenic and cadmium a canary yellow, and several, as lead, mercury, and bismuth, black or brown precipitates.

Sulphuretted hydrogen is highly inflammable; if burned in a limited quantity of air, the hydrogen is consumed, while most of the sulphur is deposited. By means of nitric acid or chlorine it may be completely decomposed; hence chlorine acts as a disinfectant and purifier of sewers or rooms impregnated with the odour of sulphuretted hydrogen. This gas is very poisonous; air being capable of producing death to large animals, if respired, though it may not contain more than $\frac{1}{800}$ of this gas. Many of the metals decompose sulphuretted hydrogen, particularly when heated in this gas, combining with the sulphur, and setting the hydrogen free. This occurs slowly, even at common temperatures; and hence metals, as gold and silver, which are not oxidized by the air, are gradually tarnished by the sulphuretted hydrogen, which, exhaled from decomposing animal matter, is always present in the atmosphere. This gas, evolved probably by the action of water on the native sulphurets of iron, at high temperatures, is a frequent constituent of mineral springs, and forms the class of spas termed sulphureous, such as those of Harrowgate, Lucan, and Golden-bridge. They are easily recognised by the fetid odour, by blackening a silver spoon, or by giving a black or brown precipitate with a solution of acetate of lead.

In its chemical relations, sulphuretted hydrogen assimilates itself closely to water; its composition and equivalent numbers are as follows:

Sulphur,	94·18	One equivalent,	=201·2 or	16·1
Hydrogen,	5·82	One equivalent,	= 12·5 or	1·0
	100·00		213·7	17·1

Bisulphuret of Hydrogen.—To prepare this substance, bisulphuret of potassium is to be dissolved in water, and the solution gently poured into dilute muriatic acid;

the potassium combines with the chlorine, and the hydrogen unites with the sulphur, $K.S_2$ and $H.Cl.$ giving $K.Cl.$ and $H.S_2$; the latter sinks to the bottom of the vessel as a heavy yellow liquid, insoluble in water, but decomposed rapidly by contact with it, unless free acid be present. It is not easily obtained pure, as the sulphuret of potassium, formed by melting salt of tartar and sulphur together, or by dissolving sulphur in a solution of caustic potash, always contains an excess of sulphur beyond two atoms, which, precipitating along with this true compound, dissolves in it, and modifies its properties and composition.

This oily liquid is characterized by separating, with great ease, into sulphuretted hydrogen gas and solid sulphur; indeed, the best way of obtaining sulphuretted hydrogen condensed into a liquid, is to seal up, in a strong tube, a quantity of this bisulphuretted hydrogen, which, after a short time, is decomposed; the gas, not being able to escape, is liquefied by the pressure it exercises, while the sulphur separates in octohedral crystals.

This body is decomposed by all substances which decompose deutoxide of hydrogen. Black oxide of manganese, or oxide of silver put in contact with it, evolve sulphuretted hydrogen gas, and often with the appearance of light and heat; it corrodes the skin. and appears to possess bleaching properties.

Sulphurets of Nitrogen have been discovered and described; they are solid and crystallizable, but are of no importance.

Of Selenium.

Selenium was discovered by Berzelius, and accompanies, although in exceedingly small quantity, the native metallic sulphurets, existing as seleniurets of the same metals. It remains even still a very rare substance: it has not been introduced into the arts or into medicine, and it will hence be necessary to touch upon its history but very slightly.

When extracted from its native combinations, selenium is a solid of a dark brown colour, and when smooth, with metallic lustre. Its density is 4·32; its fracture is crystalline; it melts a little above the boiling point of water, and boils at 650°; its vapour is of a deep yellow colour, like that of sulphur. In its manner of combination it resembles, almost completely, sulphur.

In one respect, however, they differ; when selenium is burned in air, it combines with but one equivalent of oxygen, forming *oxide of selenium* ($Se.O.$), a colourless gas, which is remarkable for its pungent odour of horseradish. By this means selenium may be recognised, even when present in exceedingly small quantity. Sulphur does not appear to form a similar compound.

When selenium is boiled with nitric acid, it unites with two equivalents of oxygen, and forms *selenious* acid, $Se.O_2$. This may be also produced by burning selenium in oxygen gas at a high temperature. It is solid, white, volatile, and may be obtained crystallized by sublimation, or from its watery solution. Selenious acid may be deprived of its oxygen by contact with zinc or iron filings, or by sulphurous acid: selenium is set free as a crimson precipitate. When selenite of ammonia is heated, it gives water, nitrogen, and free selenium.

If a current of chlorine gas be passed through a solution of selenious acid, or if selenium be melted with nitre, the *selenic acid* is formed ($Se.O_3$), which has the most remarkable analogy with sulphuric acid. All their similar salts are isomorphous, and almost identical in properties. Indeed, to distinguish them, it is necessary to boil the salt with muriatic acid, which has no action on the sulphate, but gives with the seleniate, chlorine, and selenious acid.

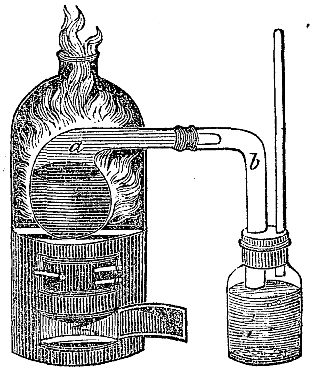
Seleniuretted Hydrogen is formed by the action of acids upon metallic seleniurets, in precisely the same manner as that described under the head of sulphuretted hydrogen. It is a colourless gas, of an extremely fetid odour, irrespirable, soluble in water, and precipitating, from the solutions of many of the metals, metallic seleniurets; these are generally black or brown; but the seleniuret of manganese is, like the sulphuret, flesh-red, and that of zinc is white.

When sulphuret of hydrogen is passed into a solution of selenious acid, water is formed, and a sulphuret of selenium is produced analogous to selenious acid, its formula being $Se.+S_2$. It is a canary yellow powder, insoluble in water.

Of Phosphorus.

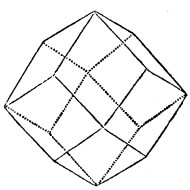
Phosphorus exists in nature, principally in the animal kingdom, in the bones of the vertebrated animals, in the fluids of the body, and also in the pulpy material of the brain and nerves. It is found in small quantity in many vegetables, and is a constituent of some minerals. It is prepared as an article of manufacture in large quantity in London and Paris. In the latter city it is computed that about 200,000 lbs. of phosphorus are annually obtained.

The principal source of phosphorus is the earthy material of bones (phosphate of lime). The bones are first burned until they become completely white, and then ground to powder. To three parts of this powder are added thirty parts of water and two of oil of vitriol. The sulphuric acid unites with a portion of the lime of the bone ashes, while the remainder forms, with the whole of the phosphoric acid, a soluble salt, which is obtained in the liquor, when the insoluble sulphate of lime is separated by straining through a cloth. The liquor is evaporated to the consistence of a sirup, and gradually mixed with a quantity of powdered charcoal, about one fourth the weight of the bones that had been used, and the whole completely dried at a temperature just below redness. The mass is introduced, in powder, into an earthen retort, *a*, which is placed in a furnace, as in the figure. To the neck of the retort is adapted a copper tube, *b*, the other extremity of which dips a little into the water in the bottle which serves as a receiver. The retort being gradually heated, the excess of the phosphoric acid is decomposed by the charcoal, the carbon of which combines with the oxygen to form carbonic acid, while the phosphorus becomes free; this being volatilized by the high temperature, passes in the state of vapour into the copper tube, where it is condensed, and, flowing down in the liquid form into the bottle, collects under the surface of the water. The copper tube must dip so little under the water, that by no condensation could this be forced back into the retort.



The phosphorus so obtained is again melted under the surface of the water, and poured into glass tubes, where it is allowed to solidify. It thus gets the cylindrical form in which it is found in commerce.

Phosphorus, when pure, is transparent and colourless; but, as generally found, it is of a pale yellow, or even of a reddish colour. At ordinary temperatures it is soft, so that it may be bent or cut with a knife; but at 32° it becomes quite brittle and crystalline in its fracture. It is insoluble in water, but it dissolves in the volatile oils, in ether, and in sulphuret of carbon, from which last it may be obtained in crystals of considerable size, which are regular dodecahedrons, as in the figure. It has also been obtained crystallized by fusion, under the form of octohedrons. At 108° phosphorus melts into a colourless liquid, and at 550° it boils, forming a colourless vapour, the sp. gr. of which is 4327. Phosphorus appears to assume an anomalous condition like that of sulphur; when strongly heated and suddenly cooled, it becomes jet black and opaque, but gradually returns to its ordinary aspect.



Phosphorus is exceedingly inflammable. Even at ordinary temperatures, when exposed to the air, it burns slowly, forming phos-

phorous acid, and emitting light visible in the dark, from whence its name (φως φερω, I bring light). It, at the same time, emits a remarkable and penetrating garlic smell. It is hence that phosphorus is used to analyze atmospheric air, and that it must always be preserved under water. When heated to 120° phosphorus bursts into brilliant flame, and unites with oxygen to form phosphoric acid. The combustibility of phosphorus is influenced by the presence of various gaseous bodies in a very remarkable degree. Thus, in pure oxygen, phosphorus does not burn nor give any light until the temperature is raised to 80°; and if the oxygen or air be mixed with small quantities of olefiant gas, or the vapours of ether or of oil of turpentine, its slow combustion may be totally prevented. This influence even extends, under some circumstances, to much higher temperatures.

The atomic weight of phosphorus had been formerly taken as 15·7 (H.=1) in consequence of some views of the constitution of its compounds, which are now generally abandoned, and I consider the true equivalent number to be 31·4, double the former.

Phosphorus combines with oxygen in four proportions, forming an oxide and three acid compounds, the constitution of which follows:

Oxide of phosphorus . . .	$=2P.+O.=62·8+8·0=70·8$
Hypophosphorous acid . . .	$=P.+O.=31·4+8·0=39·4$
Phosphorous acid	$=P.+O_3=31·4+24·0=55·4$
Phosphoric acid	$=P.+O_5=31·4+40·0=71·4$

Oxide of Phosphorus.—When phosphorus is exposed to light, in water containing air dissolved, it gradually becomes covered with a white powder, which is a compound of phosphorus with water; but there forms, at the same time, a reddish substance, which is oxide of phosphorus. It is generated, also, whenever phosphorus is incompletely burned, and may be formed in large quantity by melting phosphorus under water, and bringing a stream of oxygen gas to act upon it by means of a tube passing to the bottom of the vessel; the phosphorus burns brilliantly, but, being present in great excess, it passes principally only to the lowest degree of combination that it can form. It may be obtained purer by other processes, which are, however, too complicated to be introduced in this place.

The oxide of phosphorus so formed is a red or yellow powder, insoluble in water; it is exceedingly inflammable in some forms, but in others does not take fire until heated to near the boiling point of mercury. It is not probable that the red and yellow substances which are called oxide of phosphorus are really identical, as they differ in their most striking characters besides in colour. The formula $P_2O.$ is that obtained from the yellow matter; Pelouze considers the reddish matter to be expressed by P_3O_2.

Hypophosphorous Acid.—This acid is very little known; it is formed when phosphorus is heated in a solution of an alkali or earth: water is decomposed; one portion of phosphorus combining with the hydrogen, and another with the oxygen, produce phosphuretted hydrogen gas, which passes off, and hypophosphorous acid, which remains combined with the alkali or earth employed; the reaction may be shown thus with phosphorus and solution of barytes: 4P., 3H.O., and 3Ba.O., give $3(P.O.+Ba.O.)$ and $P.H_3$.

The hypophosphite of barytes, so obtained, may be decomposed by sulphuric acid, and the sulphate of barytes being removed by filtration, the hypophosphorous acid remains uncombined; its solution may be evaporated to the consistence of a sirup, but it cannot be obtained solid; it is decomposed, by continuing the heat, into phosphuretted hydrogen, phosphoric acid, and some phosphorus is set free.

Its salts are all soluble in water, and most of them crystallize and contain water of crystallization; when heated strongly, they give phosphuretted hydrogen and a phosphate of the base.

Phosphorous Acid.—This acid is the principal product of the slow combustion of phosphorus, but, to obtain it pure, it is necessary to avoid carefully an excess of oxygen; for this purpose, a glass tube of ten inches long and half an inch bore is

drawn out at one end to a point, with an aperture large enough to admit a pin, and bent at an obtuse angle about two inches from the point; at the bend is laid a piece of phosphorus, which is heated until it takes fire, but the temperature must not rise so high as to sublime any of it. As there is a great excess of phosphorus present, the principal product of the combustion is phosphorous acid, which, being formed in exceedingly light flakes, is carried by the current of air to the upper part of the tube, where it is deposited. These flakes are volatile, and may be sublimed from one part of the tube to another; they attract water so powerfully, that the heat evolved is sometimes great enough to inflame the phosphorous acid, which then combines with more oxygen, and forms phosphoric acid.

Phosphorous acid is more easily prepared in the liquid form; for this purpose, a quantity of phosphorus is placed in a thin glass vessel, covered with water to the depth of some inches; a current of chlorine is then conducted by a tube to the phosphorus, which inflames and forms protochloride of phosphorus; this substance is immediately decomposed by the water, phosphorous acid and muriatic acid being produced; the $P.Cl_3$ and $3H.O.$ giving $P.O_3$ and $3H.Cl.$; both acids dissolve in the water, but by evaporating the solution to the consistence of a sirup, the muriatic acid passes off as gas, and the hydrate of phosphorous acid, $P.O_3+3H.O.$, remains behind. This hydrated acid cannot be freed from water by farther heat, it being then decomposed into phosphoric acid, and the variety of phosphuretted hydrogen which is not spontaneously inflammable. Thus $4(P.O_3+3H.O.)$ give $3P.O_5+3H.O.)$ and $P.H_3$.

The solution of phosphorous acid absorbs oxygen rapidly from the air, and, with the assistance of heat, reduces to the metallic state the salts of mercury, silver, gold, and platina. It is hence occasionally used as a deoxidizing agent.

Phosphoric Acid.

When this acid is required in large quantity, it is generally prepared from the earth of bones, which are acted on by sulphuric acid, as was described for the preparation of phosphorus. The acid solution of superphosphate of lime is decomposed by carbonate of ammonia, by which the lime is thrown down in combination with carbonic acid, and the phosphoric acid remains in solution as phosphate of ammonia. This salt may be crystallized, but it is generally evaporated to dryness, and ignited; the ammonia passes off, and the phosphoric acid remains behind melted, and solidifies on cooling into a colourless glass, the *glacial* phosphoric acid.

It may also be obtained by acting on phosphorus with dilute nitric acid. This supplies oxygen to the phosphorus, and nitric oxide is evolved. When the action has terminated, the solution is to be evaporated to dryness, and the residual phosphoric acid ignited, to expel all traces of nitric acid. This process is somewhat dangerous, as sometimes fragments of phosphorus are projected by the effervescence out of the liquid, and burning in the nitric oxide gas, may burst the retort. The phosphoric acid may also be prepared very simply, and in a pure and dry state, by setting fire to some phosphorus in a little cup, and covering it with a large bell glass. The oxygen of the contained air forms phosphoric acid, which is deposited in white flakes on the inside of the glass and on the supporting plate. In all these cases, the acid so obtained is destitute of water; it is *anhydrous.*

The phosphoric acid has a great affinity for water, combining with it almost explosively. It may form three distinct compounds, *phosphates of water*, the constitution of which is as follows:

Monobasic phosphate of water . .	$P.O_5+ H.O.$
Bibasic phosphate of water . .	$P.O_5+2H.O.$
Tribasic phosphate of water . .	$P.O_5+3H O.$

This relation was first established by the researches of Graham, whose admirable memoir on the arseniates and phosphates formed an important epoch in science. The phosphoric acid combines not only with water in these three proportions, but each of them is a type of a series of salts which the phosphoric acid is capable of forming. Thus there is a class of *monobasic phosphates*, another class of *bibasic phosphates*, and a third, which is the most common, of *tribasic phosphates;* the water contained in the phosphates of water being replaced to a greater or less extent by means of equivalent proportions of ammonia or metallic oxides.

A solution of phosphoric acid in water may contain any one of the three phosphates of water that have been described, and, when neutralized by bases, may hence produce totally different salts. The properties of a solution of phosphoric acid may therefore be totally different, according to the manner in which it had been prepared, and hence this acid was at one time ranked as a remarkable instance of isomerism; but Graham has beautifully shown that the difference of properties is only the result of the existence of the different states of combination in which the phosphoric acid actually exists. It will consequently be necessary to study separately the properties of the three compounds of phosphoric acid with water.

Monobasic Phosphate of Water.—A solution of this body reacts powerfully acid; it precipitates albumen (white of egg) in white curds; when neutralized by a base, it gives salts which contain but one atom of base, their formula being $P.O_5+R.O.$, and a soluble salt of it produces, in solutions of silver, a white, soft precipitate, $P.O_5+Ag.O.$ This is the least stable of the phosphates of water; it gradually passes into the other forms, particularly when its solution is boiled.

Bibasic Phosphate of Water.—This form of the acid may be prepared by decomposing bibasic phosphate of lead by sulphuretted hydrogen. It is characterized by combining always with two equivalents of base, forming salts, whose formula is $P.O_5+2R.O.$; its salts give, with nitrate of silver, a white precipitate, $P.O_5+2Ag.O.$, which is not pasty like the monobasic phosphate. The salts of this acid may contain only one equivalent of fixed base, the other being water, and may hence, at first sight, appear to be constituted like the monobasic salts; the basic water is, however, easily known to be present, by its not being expelled by a moderate heat with the water of crystallization, but requiring a temperature approaching to ignition for its expulsion.

Tribasic Phosphate of Water.—This is the form of phosphoric acid which represents the class of salts most generally known; it is characterized by not precipitating albumen, and by combining with three equivalents of base when fully neutralized. In the majority of cases, of the three equivalents of base, one is water; thus the common phosphate of soda is a tribasic phosphate, its formula being $(P.O_5+2Na.O.H.O.)+24Aq.$; when moderately heated, or even by long exposure to dry air, it loses the 24Aq., but it requires to be melted at a red heat in order to drive off the twenty-fifth atom of water; and, if this be done, on redissolving the fused mass in water, it crystallizes in a totally different form, and is found to have been

changed into bibasic phosphate of soda, the formula of which is $(P.O_5+2Na.O.)+10Aq$. The difference is remarkably shown by the action of these salts on solution of silver; common phosphate of soda precipitates nitrate of silver of a canary yellow, and the solution becomes acid; one equivalent of tribasic phosphate of soda decomposing three equivalents of nitrate of silver, producing one equivalent of tribasic phosphate of silver, two of nitrate of soda, and one of nitrate of water; this last being liquid nitric acid, of course, renders the liquor acid. The reaction may be simply expressed:

$$P.O_5+2Na.O.H.O. \text{ and } 3(N.O_5+Ag.O.)$$
$$\text{give } P.O_5+3Ag.O. \ldots 2(N.O_5+Na.O.) \text{ and } N.O_5+H.O.$$

If, on the other hand, bibasic phosphate of soda be used, the liquor remains neutral, for $P.O_5+2Na.O.$ and $2(N.O_5+Ag.O.)$ give $P.O_5+2Ag.O.$ and $2(N.O_5+Na.O.)$.

In the tribasic phosphates it frequently occurs that there is but one equivalent of fixed base, the other two being water; such salts have frequently an acid reaction, and were formerly termed biphosphates. Thus one tribasic phosphate of soda is $P.O_5+Na.O..2H.O.$; the biphosphate of ammonia is tribasic, its formula being $P.O_5+N.H_4O..2H.O.$

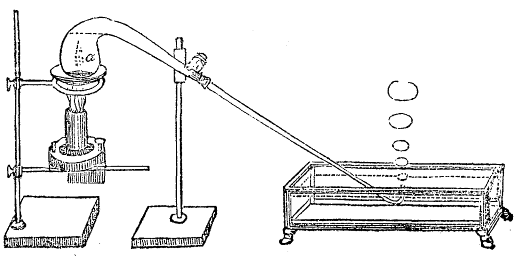
These salts of phosphoric acid were originally designated by Graham metaphosphates, pyrophosphates, and common phosphates, but the systematic names which he has since proposed should be universally adopted.

In the general remarks on the constitution of salts, and on some other occasions, I shall have opportunities to return to the consideration of this subject.

Compounds of Phosphorus and Hydrogen.

Although it is probable that there exist at least two compounds of phosphorus and hydrogen, yet I shall describe only that which is gaseous $(P.H_3)$, as of it alone do we possess accurate knowledge.

The modes of preparing this gas have been already noticed. It may be formed, 1st, when phosphorus is heated in a solution of potash or barytes, or with milk of lime; the water being decomposed, gives its oxygen to one portion of the phosphorus to form hypophosphorous acid, and its hydrogen to another, forming phosphuretted hydrogen gas: 2d, when the hydrated phosphorous acid is heated, the water is decomposed, and phosphoric acid and phosphuretted hydrogen are produced. The gas, prepared in these ways, possesses very different properties; I shall term that obtained by the first process the A, and that by the second the B variety. If the A gas, evolved from the retort *a*, be allowed to bubble through the water of the pneumatic trough, each bubble of gas, as it bursts in



the air, takes fire spontaneously, and, burning with a beautiful white flame, forms a ring of phosphoric acid smoke, which, widening as it rises, may ascend to a considerable height, if the air of the apartment be still, without its form being broken up. The structure of this ring is exceedingly curious and pretty; it consists of an amazing number of small rings, which revolve with great rapidity on their axis, and whose plane is perpendicular to that of the general ring which they produce. This is spontaneously inflammable phosphuretted hydrogen: if the gas bubbles be received in a jar of pure oxygen, the combustion is excessively brilliant and explosive. The B variety of the gas is not spontaneously inflammable, but if set on fire it burns with the same appearance as the other.

On analysis, the two varieties give exactly the same result; they are colourless and transparent, and of a very disagreeable garlic smell; but slightly absorbed by water, and precipitating the generality of metallic salts, giving insoluble phosphurets. The specific gravity is the same for both, being 1185, which arises from

One volume of phosphorus-vapour		=4327·0
and six volumes of hydrogen	68·8×6=	412·8
being condensed to four		4739·8
of which one weighs, therefore		1184·9

Their constituents by weight, and equivalent numbers, are as follows:

Phosphorus,	=91·29	One equivalent,	=392·3 or	31·4
Hydrogen,	8·71	Three equivalents,	= 37·5 or	3·0
	100·00		429·8	34·4

These two varieties were naturally looked upon as isomeric, but Graham has shown that the difference of properties may arise from the presence of a small quantity of foreign substance, as such may change the one variety into the other. Thus a very small quantity of the vapour of ether removes altogether the power of spontaneous inflammability from the A variety; the vapour of the essential oils, and even carbon, phosphoric acid, and potassium, produce the same effect. On the other hand, an exceedingly small quantity of vapour of nitrous acid or nitric oxide converts the variety B into A, and makes it spontaneously inflammable. Graham considers that, in obtaining the gas from phosphorus and milk of lime, &c., it is accompanied by a very minute trace of some compound of phosphorus and oxygen, probably the same as is formed by nitrous acid with the B variety, which is really spontaneously inflammable, and, acting as a match, inflames the general mass of gas (see p. 296.)

Phosphuret of Nitrogen.—This compound has been discovered and described by Rose, but possesses no important properties.

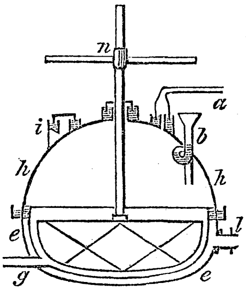
Sulphuret of Phosphorus is formed by melting together sulphur and phosphorus in equivalent weights. It appears that these elements unite in more proportions than one. The compound is much more inflammable than phosphorus, and is the material used in the phosphorus match-boxes.

Of Chlorine.

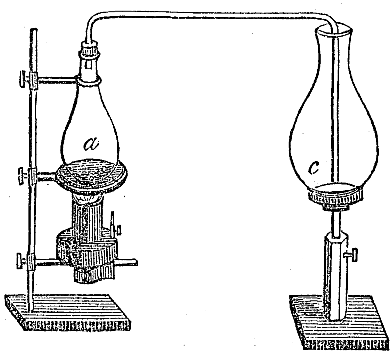
Chlorine exists in large quantity in nature, principally combined with sodium, forming immense deposites of rock-salt (chloride of

sodium) in England, in Poland, and elsewhere; and in the same state it communicates the saltness, and constitutes the chief ingredient of sea-water. It is found also combined with calcium, mercury, lead, silver, and some other metals; but these compounds are rare, and exist only in small quantity. The only source of chlorine practically useful in chemistry and in the arts is from common salt.

To obtain chlorine in large quantity, the common salt is mixed with peroxide of manganese, and then decomposed by sulphuric acid; the half of the oxygen of the peroxide of manganese passes to the sodium, the chlorine being expelled, and the soda and protoxide of manganese both unite with the sulphuric acid. Thus $Mn.O_2$ and $Na.Cl.$, treated with $2S.O_3$, produce $S.O_3 . Na.O.+S.O_3 . Mn.O.$, and $Cl.$ is evolved. By weight, about six parts of oxide of manganese and eight of chloride of sodium are employed with thirteen of oil of vitriol; and as the manufacturers of chloride of lime are generally makers of oil of vitriol also, a proportionate quantity of acid of 1·600 from the chamber (p. 289) is generally used in place of strong oil of vitriol, the expense of concentration being thus saved. Into a leaden still, *h*, *h*, such as is represented in the figure, the mixed salt and manganese are introduced at the aperture *i*, which is then tightly closed; the sulphuric acid enters by the bent funnel *b*, and these materials are well mixed by means of the agitator, turned by the cross handle *n*; the gas evolved escapes by the tube *a*, which conducts it to its destination. At first the operation does not require heat, but the still sits in an iron jacket, *e*, *e*, into which steam is conducted by the tube *l*, and thus the heat necessary for the decomposition is kept up; a waste-pipe, *g*, serves for running out the residue of one process, in order to clear the still for another.



When chlorine is required in small quantity in the laboratory, it may be more conveniently prepared from the muriatic acid of commerce, which is a solution of chloride of hydrogen gas in water. This is completely decomposed by peroxide of manganese at very moderate temperatures, the hydrogen of the muriatic acid combining with the oxygen of the peroxide of manganese to form a deutochloride of manganese, which is completely resolved by a very moderate heat into protochloride and free chlorine. Thus, at first, $Mn.O_2$ and $2Cl.H.$ give $Mn.Cl_2$ and $2H.O.$, and then $Mn.Cl_2$ separates into $Mn.Cl.$ and $Cl.$, which is evolved as gas. For this it is only necessary to introduce about one part of peroxide and three of muriatic acid into an apparatus, such as those already often figured, and the gas may be obtained. The collection of the chlorine requires some remark. It is absorbed rapidly by cold water, and it cannot be collected over mercury, as it combines rapidly with it, forming calomel; water heated to above 90° should therefore be used; but it is still better to take advantage of the great density of chlorine for its collection.



If the tube conducting the chlorine from the flask *a*, in

which it is generated, be brought to the bottom of a dry glass, *c*, the chlorine issues there, and, being much heavier than the air, pushes the air up out of its way, and gradually fills the jar completely, precisely as, by conducting a stream of water to the bottom of a vessel containing oil, this might be perfectly expelled, and the vessel filled with water. The colour of the chlorine allows the gradual filling of the bottle to be seen, and by stopping its aperture with a greased stopple, the gas may be preserved unaltered for a long time.

The chlorine, when thus prepared, is a greenish yellow gas, whence its name ($\chi\lambda\omega\rho o\varsigma$); of an extremely suffocating odour, irritating the air passages when respired, even very much diluted, in an intolerable degree. Its specific gravity is 2·470. On plunging a lighted taper into chlorine, it burns for a moment with a red, smoky flame, but is soon extinguished. Many bodies burn, however, more readily in chlorine than in air, or even in oxygen gas. If some powdered antimony or arsenic be thrown into a bottle of chlorine, they take fire, with bright scintillations. Tin or brass foil burns spontaneously, as also phosphorus, although with little light. A paper dipped in oil of turpentine takes fire spontaneously, the hydrogen burning, and the carbon being deposited as a thick black smoke. The affinity of chlorine for hydrogen is very great: when mixed, these gases gradually unite, even at common temperatures, and suddenly, with explosion if set on fire by a taper or by the electric spark. In consequence of this affinity for hydrogen, chlorine decomposes most organic substances, one half of the chlorine removing an equivalent quantity of hydrogen, and the other half going in its place; thus ether and chlorine give chloride of hydrogen and chlorine ether, $C_4H_5O.$ and $10Cl.$ giving $C_4Cl_5O.$ and $5H.Cl.$ Very often, however, the action of chlorine is much more complex.

Perhaps the most important character of chlorine, and certainly that upon which its value in the arts depends, is its power of removing the colour of organic substances; its bleaching properties. Formerly it was considered that water was necessary for this bleaching, and that the chlorine combined with the hydrogen, while the oxygen of the water, being thus thrown upon the organic substance, oxidized it, and formed a new body, which was colourless. I have shown, however, that this is not the case, but that the chlorine enters into the constitution of the new substance formed, sometimes replacing hydrogen, at others simply combining with the coloured body, and in some, the reaction being so complex that its immediate stages cannot be completely traced. I shall notice this agency of chlorine again when describing the chloride of lime, and also when discussing its relations to organic chemistry.

From this action on organic bodies, chlorine is extensively employed as a disinfectant, to remove the miasmata and infectious impurities by which the atmosphere of an hospital may be contaminated. For this purpose, it is desirable to evolve the gas slowly, but continuously; in order to do so, some chloride of lime, diffused through water, may be placed in a capsule or teacup, and by a funnel, the throat of which is partly stopped, dilute sulphuric acid be allowed to drop down on it. The acid takes the lime, and the chlorine is set free.

When chlorine is brought into contact with water at 32°, they combine, forming a hydrate which crystallizes in plates, and which, when heated to about 45°, is decomposed. If a quantity of these crystals be sealed up in a strong glass tube, the chlorine, when liberated, exercises so much pressure as to condense itself into a liquid. This was the first instance in which the liquefaction of the gases was successful. Water holding chlorine in solution possesses the colour, odour, taste, and bleaching properties of the gas itself, and may hence be used for the purposes of the arts, although not so manageable or convenient as many other forms. When chlorine water is exposed to the light, it is gradually decomposed, chloride of hydrogen being formed, and oxygen set free; the solution becomes colourless, loses its bleaching powers, and acquires an acid reaction. In contact with other bodies, chlorine may decompose water much more rapidly, and is hence frequently employed as an oxidizing agent, substances being frequently oxidized by chlorine to a higher degree than by nitric acid. This results, probably, from the chlorine first combining with the body, and the compound then decomposing water; thus, when chlorine converts selenious acid into selenic acid, it is probable that it is not that the chlorine decomposes water, but that it unites with the selenious acid, forming chloro-selenious acid, $Se.O_2 . Cl.$, which, in contact with water, is resolved into $Se.O_2 . O.$ and $Cl.H.$ Very frequently chlorine oxidizes a metal to a higher degree by combining with one portion of it, and hence throwing all of the oxygen upon the remainder; thus protoxide of iron is converted into peroxide by chlorine, because $6Fe.O.$, acted on by $3Cl.$, produce Fe_2Cl_3 and $2Fe_2O_3$. The direct decomposition of water by chlorine I consider to occur very seldom.

The combinations of chlorine form, perhaps, next to those of oxygen, the most complete series which exists in chemistry. Its affinities are so varied that it unites with almost all the simple bodies, metallic and non-metallic, and in most cases it forms more than one compound with the other body. Its metallic compounds are generally constituted like the oxides of the same metals, but in its union with the non-metallic bodies it does not appear to follow so closely the analogies of oxygen.

Chlorine possesses also the property of combining with metallic oxides, apparently without decomposition in many cases, and forming compounds resembling peroxides, in which a portion of the oxygen is replaced by chlorine. Thus, with lime it forms $Ca.O. . Cl.$, with protoxide of lead $Pb.O. . Cl.$, with barytes $Ba.O. . Cl.$, which correspond probably to $Pb.O_2$ and $Ba.O_2$. In the hydrate of chlorine, which is $Cl.+10H.O.$, it is likely that a compound corresponding to peroxide of hydrogen may exist, and that the constitution of the crystals may be $H.O. . Cl.+9H.O.$, and that bleaching compounds in general may have that type.

Chlorine is easily recognised, when free, by its peculiar odour, by its bleaching powers, and by producing with a solution of nitrate of silver a white curdy precipitate, which is insoluble in acids, soluble in water of ammonia, and is rapidly blackened by exposure to the sun's rays. When in combination with a metal, its solution gives the same kind of precipitate of chloride of silver, but the bleaching properties and smell are absent.

Compounds of Chlorine with Oxygen.

These are four, constituted as follows:

Hypochlorous acid	$=Cl.+O.=35 \cdot 4+8=43 \cdot 4$
Chlorous acid	$=Cl.+4O.=35 \cdot 4+32=67 \cdot 4$
Chloric acid	$=Cl.+5O.=35 \cdot 4+40=75 \cdot 4$
Perchloric acid	$=Cl.+7O.=35 \cdot 4+56=91 \cdot 4$

Hypochlorous Acid.

If red oxide of mercury, diffused through a small quantity of water, be introduced into bottles containing chlorine, and the whole be agitated, the gas is rapidly absorbed, and, combining with both constituents of the oxide, forms chloride of mercury and hypochlorous acid. Thus Hg.O. and 2Cl. give Hg.Cl. and Cl.O. As there is always an excess of oxide of mercury employed, the chloride of mercury combines with it, forming the insoluble brown oxychloride of mercury Hg.Cl.+3Hg.O., which separates, and the hypochlorous acid remains nearly pure in solution in the water. By a very moderate heat it may be distilled in a dilute form, and so obtained quite pure from sublimate, but at 212° the acid is rapidly decomposed into chlorine and oxygen.

A solution of hypochlorous acid is yellow; its odour is like that of chlorine; it bleaches powerfully; it decomposes spontaneously even in the cold, forming chlorine and chloric acid; it oxidizes most bodies with extreme energy. To obtain it in the gaseous form, it is sufficient to introduce a small quantity of the solution into a tube over mercury, and to add pieces of dry nitrate of lime; the water is absorbed by this deliquescent salt, and the acid remains as a greenish yellow gas, very similar to chlorine in all respects; water absorbs 100 volumes of it; by raising its temperature even slightly, it explodes, and its volume is increased by one half: 100 volumes of it produce 100 of chlorine and fifty of oxygen. Its specific gravity is by theory 3021·3, and its equivalent numbers 542·6 or 43.4: its formula is Cl.O.

The hypochlorous acid combines with bases to form salts, hypochlorites, which possess the bleaching properties of the acid in a great degree; but their nature is involved so much in the general history of the bleaching compounds of chlorine, that I shall not enter upon any notice of them here.

Chloric Acid.

When chlorine is brought into contact with an alkaline solution, it is absorbed with great avidity, and the liquor acquires powerful bleaching properties. Concerning the nature of the reaction, the opinions of chemists are not completely settled; it may be supposed, on the one hand, that the chlorine unites directly with the alkali, forming simply, if potash be employed, chloride of potassa, K.O. . Cl. But, on the other hand, it is possible that a quantity of alkali may be decomposed, as certainly occurs with oxide of mercury, and that chloride of potassium and hypochlorite of potash may coexist in the liquor; thus, that 2K.O. and 2Cl. should produce K. Cl. and Cl.O.+K.O. The majority of chemists incline to the latter view, but the subject will hereafter receive detailed consideration.

In any case, this bleaching alkaline liquor is completely decomposed by boiling, particularly if it be very concentrated. Oxygen is then evolved in considerable quantity, while chloride of potassium and chlorate of potash are produced: thus $9(K.O.+Cl.O)$ evolve $12O.$, and form $8K.Cl.$ and $K.O.+Cl.O_5$. It is in this way that the chlorate of potash of commerce is obtained, and from it the chemist prepares chloric acid.

A solution of this acid is readily prepared by decomposing a solution of chlorate of barytes by sulphuric acid. It cannot be obtained solid, as, when a concentrated solution of it is heated, it is resolved into chlorine, oxygen, and perchloric acid. It does not bleach; it does not precipitate a solution of nitrate of silver: when in its strongest form, of a thick, oily consistence, it sets fire to many organic bodies, and is a powerful oxidizing agent.

The compounds of chloric acid are easily recognised, by yielding, when heated, oxygen and a metallic chloride; thus the chlorate of potash is used in the preparation of oxygen (p. 244), $Cl.O_5+K.O.$ giving $Cl.K.$ and $6O.$ When mixed with sulphur and rubbed in a warm mortar, they explode, and if thrown upon an ignited coal, they deflagrate with violence.

The chlorate of potash is of very great commercial importance, from its utility in making matches, and is the source from whence the chemist obtains the remaining compounds of chlorine and oxygen.

The constitution and equivalent numbers of chloric acid are as follows: by weight,

Chlorine,	46·95	One equivalent,	=442·6	or 35·4
Oxygen,	53·05	Five equivalents,	=500·0	or 40·0
	100·00		942·6	75·4

Its formula is $Cl.O_5$, and, like the nitric acid, which it resembles in so many other properties, it consists of five volumes of oxygen united to two of the other element.

Chlorous Acid.—When chlorate of potash in fine powder is decomposed by moderately strong sulphuric acid, the chloric acid, at the moment of being set free, breaks up into two other compounds, one containing more, and the other less oxygen, the former being the chlorous, and the latter the perchloric acid, $3Cl.O_5$ giving $2(Cl.O_4)$ and $Cl.O_7$. This process must be conducted very cautiously, and the retort warmed very gently in a water bath. The chlorous acid may be collected over mercury, or, from its great density, like chlorine, in a dry jar; there remains in the retort a mixture of bisulphate and of perchlorate of potash.

This acid gas is of a rich yellowish-green colour, and an aromatic odour; it is rapidly absorbed by water; it bleaches strongly, and is a powerful oxidizing agent, its elements separating from the slightest causes. If it be heated above 212°, it explodes with a flash of light; phosphorus immersed in it takes fire spontaneously, and burns brilliantly in the mixture of chlorine and oxygen which results from its decomposition. This may be very well shown by placing some crystals of chlorate of potash and some phosphorus together, at

the bottom of a tall glass filled with water, and conducting to the mixture, by means of a long glass funnel, some oil of vitriol; the phosphorus burns in each bubble of chlorous acid gas which forms, and a brilliant combustion under water results.

When this gas is decomposed, 100 volumes produce 150, of which 50 are chlorine and 100 oxygen; its specific gravity may therefore be calculated to be 2337·5.

The chlorous acid combines with bases to form salts, chlorites, which possess bleaching properties, but are not of much importance, as they do not enter into practical use.

Perchloric Acid.—This acid is formed in the process for obtaining chlorous acid, as already described, and is obtained by washing the saline residue with cold water. The bisulphate of potash readily dissolves, leaving behind the perchlorate of potash, which is but sparingly soluble therein; this may then be dissolved in boiling water, from which it crystallizes as the solution cools. When the object is only the preparation of perchloric acid, and not of chlorous acid, the process becomes easier by heating chlorate of potash with dilute nitric acid; the elements of the chlorous acid are then separated, merely mixed together, and the explosions and sputtering which occur with sulphuric acid are avoided.

In the process of obtaining oxygen from chlorate of potash, there occurs a period at which it is necessary to elevate the temperature very much in order to keep up the evolution of gas; this arises from the salt being at first decomposed into oxygen, chloride of potassium, and perchlorate of potash, $3(K.O.Cl.O_5)$ giving $2(Cl.K.)$ and $K.O.Cl.O_7$, while 8O. are evolved as gas. This is exactly half of the oxygen which the salt contains. If the saline mass then remaining be washed with a small quantity of water, the chloride of potassium dissolves, and the perchlorate of potash remains behind.

Perchloric acid may be prepared from this potash salt by mixing it in a retort with half its weight of oil of vitriol, and as much water, and distilling; the acid passes over with the water. If it be distilled with an excess of oil of vitriol, it may be obtained free from water, and is then a white crystalline mass, very deliquescent, and evolving great heat when mixed with water. In this process, however, a great part of the acid is decomposed.

The perchloric acid is the most stable compound of chlorine and oxygen. It is not decomposed by muriatic acid, by which the chloric acid is immediately decomposed, a mixture of chlorous acid and chlorine being evolved; $Cl.O_5$ and $Cl.H.$ giving $H.O.$ and a mixture of $Cl.O_4$ with Cl., which was described by Sir Humphrey Davy as a peculiar gas, *Euchlorine.* By this means the salts of perchloric and of chloric acid may be distinguished. It is not decomposed by alcohol, nor has it any spontaneous action on organic bodies. It is well characterized by the very sparing solubility of its potash salt, whence it has been employed as a reagent to detect that alkali.

The constitution and equivalent numbers of perchloric acid are as follows:

Chlorine,	38·74	One equivalent,	=442·6	or 35·4
Oxygen,	61·26	Seven equivalents,	=700·0	or 56·0
	100·00		1142 6	91·4

Compound of Chlorine and Hydrogen.

This compound exists naturally as a gas, of which a solution in water has been known since a very early period in chemistry under the names of spirit of salt, marine acid, muriatic acid, hydrochloric acid, and, more properly, chloride of hydrogen. In speaking of it under ordinary circumstances, I shall use the common names of liquid or gaseous muriatic acid, according as it is free or combined with water; but in cases where its functions in combination are discussed, I shall term it chloride of hydrogen.

To prepare the gaseous muriatic acid, a small quantity of the commercial spirit of salt may be placed in a flask or retort connected with the mercurial pneumatic trough, and the gas, which passes off on the application of heat, collected. It may also be prepared by the action of oil of vitriol on common salt; water being decomposed, its oxygen unites with the sodium, forming soda, which combines with the sulphuric acid, while its hydrogen, uniting with the chlorine, produces the chloride of hydrogen, which is given off as a gas; the reaction may be thus expressed: $S.O_3H.O.$ and $Na.Cl.$ give $S.O_3Na.O.$ and $H.Cl.$

This gas may also be formed by putting together chlorine and hydrogen in equal volumes. Even in diffuse light they combine completely in some hours, but in the direct sunshine the union is instant and explosive. The mixture may also be fired by the taper or by the electric spark; the colour of the chlorine disappears, and the resulting muriatic acid gas occupies the same volume as its ingredients. In almost all cases of the action of chlorine on organic matters, this substance is also formed; indeed, the agency of chlorine in bleaching, and in decomposing organic compounds, appears generally to result from its disposition to unite with hydrogen.

The chloride of hydrogen is a colourless and invisible gas. When completely dry it has no action on vegetable colours, but if a trace of moisture be present it reddens litmus paper, and restores the colour of turmeric paper that has been browned by an alkali; hence it is generally looked upon as a powerful acid. When mixed with damp air it forms heavy white fumes by uniting with the watery vapour, and condensing in minute drops of liquid acid. It may be liquefied by great pressure. It cannot be breathed, but does not produce anything like the suffocating effects of chlorine.

When muriatic acid gas is put in contact with a metallic oxide, both are decomposed, a metallic chloride and water being produced; thus $Cu.O.$ and $H.Cl.$ give $Cu.Cl.$ and $H.O.$ If any of the more oxidable metals, as iron, zinc, or potassium, be heated in a current of the gas, it is decomposed, a metallic chloride being formed and hydrogen gas evolved. This occurs, also, when these metals are immersed in the liquid acid; a copious effervescence is produced by the escape of hydrogen, and the water holds a chloride of the metal in solution. In this way muriatic acid may be proved to consist of equal volumes of hydrogen and chlorine united without condensation. Its specific gravity is, by theory,

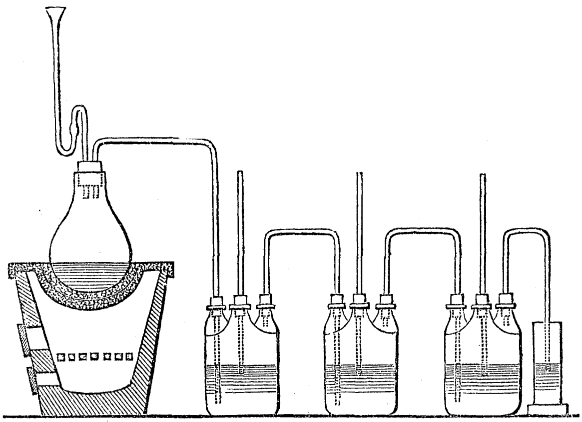
One volume of chlorine	=2470·0
One volume of hydrogen	= 68·8
give two volumes of muriatic acid	=2538·8
of which one weighs, therefore	1269·4

Its constitution and equivalent numbers are therefore,

Chlorine,	97·26	One equivalent,	=442·6 or	35·4
Hydrogen,	2·74	One equivalent,	= 12·5 or	1·0
	100·00		455·1	36·4

This gas is distinguished by its great affinity for water. If a jar of it be opened under water, this fluid rushes in, as if it were into a vacuum. If a fragment of ice be introduced into a bell glass of the gas, over mercury, the ice instantly melts, and the mercury rises in the tube, the gas being totally absorbed. The solution of the gas in water is one of the most valuable agents in chemical research.

To prepare liquid muriatic acid in the laboratory, chloride of sodium is to be introduced into a glass globe, placed in a sand-bath on the furnace, and then an equal weight of sulphuric acid and water, mixed together, are to be introduced by the funnel: the decomposition proceeds as already explained, and the gas evolved passes



by the tube into the first of a range of three-necked bottles, as in the figure. Each bottle is about half full of water. When that in the first has become completely saturated with the gas, this passes into the second, and when it has been saturated, into the third. The vertical tube in the central neck of each bottle is a safety-tube, the action of which is as follows. If a sudden condensation occurred in the first bottle, the acid in the second might, by the greater pressure on its surface, be forced back into it; but, before it can rise so high as to pass through the connecting tube, the external air enters by the safety-tube, being driven in by the difference of pressure inside and outside, and thus restores the equilibrium. Pure muriatic acid may be much more conveniently prepared for laboratory use by rectifying the spirits of salt of commerce. When this is placed in a distilling apparatus, arranged as that figured in p. 278, and about one fourth as much water is introduced into the receiver to condense the quantity of gas which is first expelled, the distillation may be carried on until the retort is nearly empty, and an acid so obtained completely pure, and of a very convenient strength for the general range of applications.

The manufacture of this acid is carried on on a very large scale more generally with a view to the extraction of the alkali from the residual sulphate of soda than for the sake of the muriatic acid, the great difficulty in a soda factory being how to get rid of the muriatic acid which is produced. When the object is, however, to prepare the

liquid acid, precisely the same apparatus is employed as for the manufacture of nitric acid, which has been already figured and described (p. 278), the cylinders being somewhat larger, as from four to five cwts. of common salt are generally decomposed in each cylinder at a charge; the upper part of the cylinder is generally, both in this operation and in the making of nitric acid, protected from the too corrosive action of the acid vapours by being lined internally with thin fire-tiles, and the heads *e e* in the figure are very frequently constructed, not of metal, but of freestone or of granite. In the decomposition of the salt upon this large scale, the oil of vitriol is employed of the strength to which it is brought in the chambers, without concentration, and in such quantity that for each equivalent of chloride of sodium an equivalent of real sulphuric acid is employed. The strongest liquid muriatic acid, thus prepared, possesses a specific gravity of 1·211. In order to obtain water fully saturated with the gas, it must be kept near the freezing point by artificial cold; it then absorbs 480 times its volume, and increases in bulk by about one fifth. Its constitution is quite definite, for in this state it consists of H.Cl.+6H.O., or in numbers,

Muriatic acid	. 40·27	One equivalent .	=455·1	or 36·4
Water . . .	. 59·73	Six equivalents .	=675·0	or 54·0
	100·00		1130·1	90·4

When this concentrated acid is heated, it evolves a large quantity of gas, and the boiling point gradually rises to 230°, at which temperature the residual acid distils over unchanged; it then has a specific gravity of 1.094, and consists of H.Cl.+16H.O., or in numbers,

Muriatic acid	. 20·13	One equivalent . . .	= 455·1	or 36·4
Water . . .	. 79·87	Sixteen equivalents . .	=1800·0	or 144.0
	100·00		2255·1	180·4

Graham has found that the strong acid, when evaporated in the open air, abandons a quantity of gas, while the remaining liquid becomes H.Cl +12H.O.

The metallic character of hydrogen, and the analogy of its combinations with those of zinc, are completely shown by comparing the formulæ of the compounds of oxide and chloride of hydrogen with the compounds of oxide and chloride of zinc, and their combinations with water. Thus I have shown that the hydrates of oxychloride of zinc are as follows:

Zn.Cl.+6Zn.O.
Zn.Cl.+6Zn.O.+ 6Aq.
Zn.Cl.+6Zn.O.+10Aq.

and the definite states of liquid muriatic acid are

H.Cl.+6H.O.
H.Cl.+6H.O.+ 6Aq.
H.Cl.+6H.O.+10Aq.

As we proceed, other similar proofs of the electro-positive and metallic character of hydrogen will be found.

The other degrees of strength of the liquid muriatic acid are solutions in water of one or other of these definite compounds; a table of them will be found in the appendix.

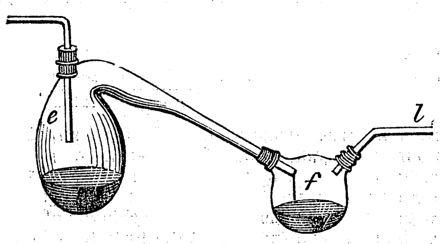
The muriatic acid of commerce frequently contains sulphuric acid, and always a trace of iron, derived from the metal cylinders in which it is fabricated. Occasionally, sulphurous acid is formed in it in small quantity. These impurities are detected thus: by diluting the muriatic acid with water, and adding nitrate of barytes, a white precipitate is formed if sulphuric acid be present; yellow ferroprussiate of potash indicates the existence of iron; while solution of protochloride of tin produces a brown precipitate of sulphuret of tin if sulphurous acid had been present.

Muriatic acid is easily recognised, as a gas, by its action on moist litmus paper, its fuming in the air, its forming with ammonia dense

white clouds of sal ammoniac, and in solution, by giving with nitrate of silver a curdy white precipitate, which blackens on exposure to light, is totally insoluble in nitric acid, but dissolves easily in water of ammonia.

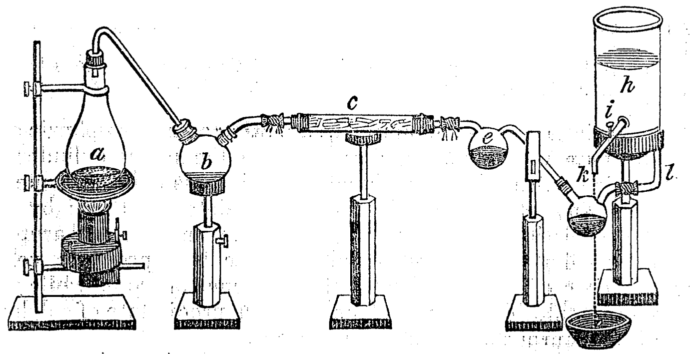
Nitromuriatic Acid. Aqua Regia.—When nitric and muriatic acids, both colourless, are mixed together, the mixture becomes deep yellow, and exhales a strong smell of chlorine and of nitrous acid, H.Cl. and $N.O_5$ giving Cl. and $N.O_4$, with formation of H.O. This decomposition, however, proceeds only so far as to saturate the liquid with chlorine; but if a metal be placed in the liquid it unites with the chlorine, and new quantities of the acid are decomposed. Thus the nitromuriatic acid is a source of chlorine in a very concentrated state, and is hence employed to dissolve gold and platina, which are not soluble in nitric acid, and to oxidize some bodies (metallic sulphurets) which resist the action of nitric acid. The name *aqua regia* was given to it from its power of dissolving gold, the ancient *rex metallorum*.

Chloride of Sulphur.—In order to obtain this body, a quantity of sulphur is placed in a tubulated retort, into which a current of chlorine gas is conducted by means of the bent tube *e*, in the figure. The chlorine and sulphur unite to form a volatile reddish yellow liquid, which distils over, and condenses in the receiver *f*, which must be kept very cool; any uncondensed gas is conducted away by the tube *l*. The chloride of sulphur, thus obtained, has always an excess of sulphur dissolved in it, from which it may be freed by a second distillation. Its specific gravity is 1·687. When exposed to the air it gives off very acrid fumes; it boils at 280°; the specific gravity of its vapour is 4686. It consists of one equivalent of chlorine united to two of sulphur, $S_2Cl.$, and in contact with water, muriatic acid, sulphur, and hyposulphurous acid are formed by mutual decomposition.



It is probable that there is another chloride of sulphur consisting of one equivalent of each, S.Cl.

Chlorides of Phosphorus.—Chlorine unites with phosphorus in two proportions, forming a liquid protochloride, $P.Cl_3$, and a solid perchloride, $P.Cl_5$. These may be prepared in a simple apparatus, like that used for chloride of sulphur; but as a



more complex arrangement is necessary for examining the action of chlorine upon many substances that will be described hereafter, I will introduce the description

of it here. The chlorine is generated by liquid muriatic acid and peroxide of manganese, in the flask *a*, supported on a sand-bath over the lamp; from it a bent tube passes to the receiver *b*, in which a quantity of watery vapour is condensed, and serves to absorb any muriatic acid gas that might escape decomposition. The pure chlorine passes then through the tube *c*, which is filled with fragments of fused chloride of calcium, which, from its great affinity for water, dries the gas completely. In the bulb *e* is contained the substance to be acted on by the chlorine, and the product of the reaction, if volatile, distils over into the receiver *k*, in which it condenses; the excess of chlorine escapes by the tube *l*, and a stream of water from the reservoir *i h* retains the receiver *k* at the temperature proper for condensation.

The phosphorus being placed in the bulb *e*, takes fire on the arrival of the chlorine gas, and continues burning until it is all converted into the liquid chloride which collects in *k*. While there is an excess of phosphorus, the protochloride is principally formed; but after all the phosphorus has been consumed, if the current of chlorine be continued, it is absorbed by the liquid in *k*, which changes into the solid perchloride.

The *Protochloride of Phosphorus* is obtained pure by stopping the process before all the phosphorus has been consumed, and rectifying the colourless liquid by distilling it in a retort containing some bits of phosphorus, which bring back any perchloride it might contain dissolved, to the state of protochloride. This body is heavier than water, by which it is completely decomposed, $P.Cl_3$ and $3H.O.$ giving $P.O_3$ and $3H.Cl.$ It is thus that the liquid phosphorous acid is obtained, as described in p. 297.

The *Perchloride of Phosphorus* is a white solid, volatile under 212°, and condensing in a crystalline form. In contact with water, it is decomposed with the evolution of great heat, producing phosphoric acid and muriatic acid, $P.Cl_5$ and $5H.O.$ giving $P.O_5$ and $5H.O.$; the sp. gr. of its vapour is 4788, consisting of ten volumes of chlorine and one of vapour of phosphorus, the eleven being condensed to six.

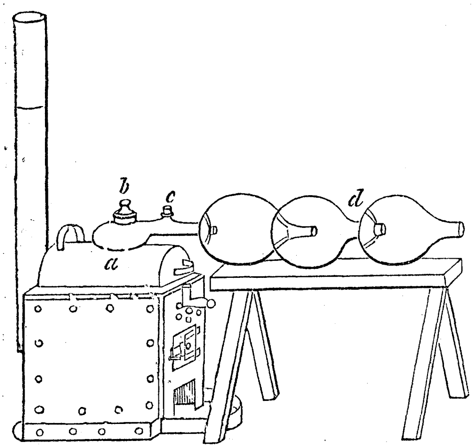
There is a *Chloride of Selenium* analogous in general properties to the chloride of sulphur.

Iodine.

Iodine is found principally in sea-water, associated with chlorine, combined with sodium and magnesium. It has been also discovered in the mineral kingdom, united with silver. For the purposes of commerce it is always extracted from *kelp*, which is a semifused mass of saline ashes remaining after the burning of various species of fuci (sea-weed).

For this purpose, the powdered kelp is lixiviated in water, to which it yields about half its weight of salts. The solution is evaporated down in an open pan, and when concentrated to a certain point, begins to deposite its soda-salts, namely, common salt, carbonate and sulphate of soda, which are removed from the boiling liquid by means of a shovel pierced with holes like a colander. The liquid is afterward run into a shallow pan to cool, in which it deposites a crop of crystals of chloride of potassium; the same operations are repeated on the mother-ley of these crystals until it is exhausted. A dense, dark-coloured liquid remains, which contains the iodine, in the form, it is believed, of iodide of sodium, but mixed with a large quantity of other salts, and this is called the iodine ley.

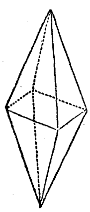
To this ley, sulphuric acid is gradually added in such quantity as to leave the liquid very sour, which causes an evolution of carbonic acid, sulphuretted hydrogen, and sulphurous acid gases, with a considerable deposition of sulphur. After standing for a day or two, the ley so prepared is heated with peroxide of manganese, to separate the iodine. This operation is conducted in a leaden retort,



a, of a cylindrical form, supported in a sand-bath, which is heated by a small fire below. The retort has a large opening, to which a capital, *b*, *c*, resembling the head of an alembic, is adapted, and luted with pipe-clay. In the capital itself there are two openings, a larger and a smaller, at *b* and *c*, closed by leaden stoppers. A series of bottles, *d*, having each two openings, connected together, as represented in the figure, and with their joinings luted, are used as condensers. The prepared ley being heated to about 140° in the retort, the manganese is then introduced, and *b c* luted to *a*. Iodine immediately begins to come off, and proceeds on to the condensers, in which it is collected; the progress of its evolution is watched by occasionally removing the stopper at *c*; and additions of sulphuric acid or manganese are made by *b*, if deemed necessary. This description of the manufacture of iodine upon the large scale at Glasgow is due to Professor Graham.

In this operation, the peroxide of manganese will be in contact at once with hydriodic, hydrochloric, and sulphuric acids; but for success, the quantity of sulphuric acid must be sufficient only to decompose the iodides, but not the chlorides. If both were decomposed, the chlorine and iodine simultaneously evolved would unite to form chloride of iodine, by which the iodine would be lost; but as the chlorine remains combined, the action becomes simply, that the metal of the iodide present is oxidized by the oxide of manganese, and the iodine set free; thus, with iodide of sodium, $S.O_3+Mn.O_2$ and Na.I. give $Mn.O..S.O_3.Na.O.$ and I.

Another mode of preparing iodine consists in adding to the solution containing iodide of sodium, a solution of sulphate of copper, in which the copper is reduced to the state of sub-oxide (Cu_2O.) by means of protosulphate of iron dissolved along with it. By the interchange of elements, sulphate of soda is formed, and a sub-iodide



of copper of a very pale yellow colour, and quite insoluble in water, is produced, $S.O_3+Cu_2O.$ and Na.I. giving $S.O_3+Na.O.$ and Cu_2I. This last is then decomposed by peroxide of manganese and sulphuric acid, as in the former process: in this way the various crystallizations described above may be avoided.

Iodine exists generally in crystalline scales of a bluish black colour and metallic lustre. It may also be obtained from solution, in the form of oblique octohedrons with a rhomboidal base, as in the figure, or in prisms. The density of

iodine is 4·948; it fuses at 225°, and boils at 347°; but it evaporates at the usual temperature, and more rapidly when damp than when dry, diffusing an odour having considerable resemblance to chlorine, but easily distinguished from it. Iodine stains the skin of a yellow colour, which, however, disappears in a few hours. Its vapour is of a splendid violet colour, which is seen to great advantage when a scruple or two of iodine is thrown at once upon a hot brick. Hence its name, from Ιοειδης, violet-coloured. The vapour of iodine is one of the heaviest of gaseous bodies, its density being 8707·7, according to calculation from its atomic weight.

Pure water dissolves about 1-7000th of its weight of iodine, and acquires a brown colour. In general, iodine comports itself like chlorine, but its affinities are much less powerful. Iodine is soluble in alcohol and ether, with which it forms dark reddish-brown liquors; solutions of iodides, too, all dissolve much iodine.

A solution of starch forms an insoluble compound with iodine, of a deep blue colour, the production of which is an exceedingly delicate test of iodine. If the iodine be free, starch produces at once the blue precipitate; but if it be in combination as a soluble iodide, no change takes place till chlorine is added to liberate the iodine. If more chlorine, however, be added than is necessary for that purpose, the iodine is withdrawn from the starch, chloride of iodine formed, and the blue compound destroyed. The iodide of starch, in water, becomes colourless when heated, but recovers its blue colour if immediately cooled. The soluble iodides give, with nitrate of silver, an insoluble iodide of silver, of a pale yellow colour, insoluble in ammonia; with salts of lead, an iodide of a rich yellow colour; and with corrosive sublimate, a fine scarlet iodide of mercury.

Iodine combines with most of the non-metallic bodies, and with all the metals, forming compounds which possess the closest similarity to the analogous compounds of chlorine. It is employed in the laboratory for many chemical preparations, and as a test of starch and for several metals.

Compounds of Iodine and Oxygen.

Iodine appears to combine with oxygen in three proportions, forming the *iodous acid*, the *iodic acid*, and the *periodic acid*. Of the constitution of the first there is nothing positively known; it has not been isolated, and the substances that have been supposed to contain it may also be considered as compounds of an iodide with an iodate. The description of these compounds will be found in the chapter on the salts; and I shall, therefore, at present, only notice the other two acids.

Iodic Acid.—This acid may be very easily prepared by boiling iodine in fuming nitric acid until it is all dissolved, and then distilling off the excess of acid; the iodic acid remains as a white crystalline mass, which deliquesces in the air. If the quantity of iodine be large, this process would occupy a very long time; and a much shorter, though more complex method is the following: The iodine being diffused through water, a current of chlorine is passed through it until all iodine is dissolved; the acid liquor so obtained is to be neutralized by carbonate of soda, by which a quantity of iodine is

precipitated; the chlorine is then passed through until this iodine disappears, and then more carbonate of soda added, and this alternation continued until the addition of the carbonate of soda produces no deposite of iodine; the solution contains then iodate of soda and chloride of sodium, generated by the decomposition of the soda by the chloride of iodine first formed. Thus 5Cl. and I. produce $I.Cl_5$, which, with 6Na.O., give 5Na.Cl. and $Na.O.+I.O_5$. This solution is then mixed with a solution of a salt of barytes, and iodate of barytes precipitates, which may be decomposed by boiling it for some time with one fourth its weight of oil of vitriol and $1\frac{1}{2}$ times its weight of water; the sulphate of barytes may be then separated by the filter, and the solution of iodic acid evaporated gently to dryness.

Iodic acid is very soluble in water; from a strong solution it crys tallizes in rhombic plates and octohedrons. When heated strongly, it separates into iodine and oxygen. It first reddens, and then bleaches litmus paper. It acts as powerfully as nitric acid in oxidizing the metals. When mixed with solution of sulphurous acid, water and sulphuric acid are formed, and iodine is set free; with sulphuretted hydrogen it gives water and iodide of sulphur. By an excess of these agents, the iodine is finally converted into iodide of hydrogen. By these means the iodic acid may be recognised, and also by its peculiar action upon morphia, which it decomposes, iodine being set free. This is more valuable as a character of morphia than of iodic acid.

The salts of iodic acid resemble the chlorates in most respects, and, like them, when heated, separate into oxygen and a metallic iodide. One mode of preparing the iodide of potassium of commerce is founded on this property. Iodine is dissolved in a solution of potash, and, when dried down, gives a mixture of 5K.I. and $I.O_5$. K.O. When this mass is fused, oxygen is given off in abundance, and ultimately pure K.I. remains. The commercial salt prepared in this way has been shown by Mr. Scanlan frequently to contain iodate of potash, either fradulently or accidentally, left undecomposed.

The composition and equivalent numbers of the iodic acid are as follows, its formula being $I.O_5$:

Iodine,	75·96	One equivalent,	=1579·5 or	126·6
Oxygen,	24·04	Five equivalents,	= 500·0 or	40·0
	100·00		2079·5	166·6

Its elements are united in the proportion, by volume, of two volumes of vapour of iodine to five volumes of oxygen.

Periodic Acid, $I.O_7$.—If a solution of iodate of soda be mixed with a great excess of caustic soda, and acted upon by a current of chlorine, a quantity of the soda is decomposed; its sodium combining with the chlorine, while its oxygen, being added to the iodic acid, converts it into the periodic acid, which combines with two equivalents of soda. Thus, 2Cl. acting on 3Na.O. and $I.O_5+Na.O.$, produce 2Na.Cl. and $I.O_7+2Na.O.$ On adding to the solution of this salt nitrate of silver, a basic periodate of silver is produced, which, being dissolved in nitric acid, gives yellow crystals of neutral periodate of silver. When put in contact with water, these crystals are decomposed, half of the periodic acid precipitating with the whole of the oxide of silver as the insoluble salt, $I.O_7+2Ag.O.$, while the other half of the acid remains in solution quite pure, and by evaporation may be obtained as a white crystallized mass.

This acid is more stable than the iodic acid; it resists a higher temperature

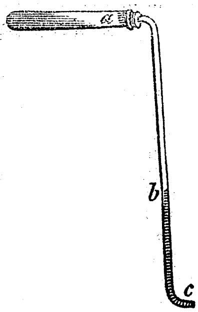
without decomposition. All its important characters may be inferred from the method of preparation.

Its composition and equivalent numbers are,

Iodine,	69·31	One equivalent,	=1579·5 or	126·6
Oxygen,	30·69	Seven equivalents,	= 700·0 or	56·0
	100·00		2279·5	182·6

Compound of Iodine and Hydrogen. Hydriodic Acid.

There is but one compound of iodine with hydrogen: this exists under ordinary temperatures and pressure as a colourless gas, which may be best generated in the following manner: Some iodine and small fragments of phosphorus are to be put together at the bottom of a glass tube, then covered with pounded glass, and gently heated, so as to produce combination. Iodide of phosphorus is thus formed. If a little water be now poured on the pounded glass, it filters through to the bottom, and there, acting violently on the iodide of phosphorus, is decomposed; from P.I. and H.O. there are produced P.O. and H.I. To the mouth of the tube may be adapted, by a cork, a smaller tube, bent as in the figure, and the hydriodic acid gas issuing from it may be collected. This gas is obtained by the method of displacement, as has been described for chlorine (p. 302); and as it fumes like muriatic acid in contact with the air, it can easily be recognised when the bottle is full.



The specific gravity of this gas is 4385, produced by

One volume of vapour of iodine	=8701·0
One volume of hydrogen	= 68·8
united without condensation	8769·8
and one volume weighing, therefore	4384·9

To obtain hydriodic acid dissolved in water, the simplest process is to act on iodine, diffused through water, by sulphuretted hydrogen gas. The iodine combines with the hydrogen, and the sulphur is set free. When the iodine has all disappeared, the liquor should be well boiled, to drive off the excess of sulphuretted hydrogen, and then filtered; the liquid hydriodic acid may be evaporated to a sp. gr. of 1·700: it is then in its strongest form, and may be distilled unaltered. Liquid hydriodic acid reddens litmus paper strongly; it dissolves iodine in large quantity; it is decomposed by all the oxidable metals, and even by mercury; and hence the gaseous acid cannot be collected over mercury. Exposed to the air, it rapidly absorbs oxygen, water being formed, and iodine being set free. It is decomposed by sulphuric acid, sulphurous acid and iodine being produced; also by nitric acid and by chlorine.

Hydriodic acid may also be obtained by acting on iodide of barium with dilute sulphuric acid.

Its composition and equivalent numbers are as follows:

Iodine,	99·22	One equivalent,	=1579·5 or	126·6
Hydrogen,	0·78	One equivalent,	= 12·5 or	1·0
	100·00		1592·0	127·6

A solution of hydriodic acid or of a metal produces, with nitrate of silver, a curdy pale yellow precipitate, which is insoluble in acids and in water of ammonia; by this character the iodides are distinguished from the chlorides, even without the action of starch upon the iodine when set free.

Iodine and sulphur may be melted together in equivalent proportions, and, on cooling, form a steel-gray crystalline mass, *iodide of sulphur*, which is decomposed gradually by exposure to the air, and appears to be rather a mixture than a true compound of its elements.

When iodine and phosphorus are warmed together very gently, they combine, evolving considerable heat, and forming *iodides of phosphorus*, the constitution of which depends on the proportions used; there appears to be at least three: the first fuses at 212°, is orange coloured, and gives, when decomposed by water, hydriodic and hypophosphorous acids; its composition is therefore P.I.: the second is gray; it fuses at 84°, and gives, with water, hydriodic and phosphorous acids; its formula is hence $P.I_3$. The third, which produces, when decomposed by water, hydriodic acid and phosphoric acid, consists of $P.I_5$, is black, and melts at 114°.

Hydriodic acid combines with phosphuretted hydrogen, forming a white solid compound, the constitution of which is of considerable interest. It cannot be prepared directly, as the gases are without action on each other except when in their nascent form. It is best prepared by introducing eight parts of iodine, two of phosphorus, and one of water, into a retort, mixed with some coarsely-powdered glass; to the neck of the retort is adapted a wide glass tube with a cork, through which a small tube passes and dips into some water. On applying heat, the phosphorus and iodine unite, and the iodide of phosphorus being instantly decomposed by the water, hydriodic acid and hypophosphorous acid are produced, which last is resolved, by contact with the water at that temperature, into phosphorous acid and phosphuretted hydrogen. This last immediately unites with the hydriodic acid, and the compound formed condenses in the neck of the retort in well shaped crystals, which, by a proper management of the heat, may be driven into the wide glass tube to be preserved. The excess of hydriodic acid gas is conducted off by the small tube, and condensed in the water.

This body was supposed to crystallize in cubes, and to be isomorphous with hydriodate of ammonia, to which this formula, in one way, might assimilate it, $H.I.+P.H_3$ corresponding to $H.I.+N.H_3$, the difference being only that phosphorus replaced nitrogen. It will, however, be shown fully, in the division on organic chemistry, that ammonia is not mere nitruret of hydrogen, $N.H_3$, but that it contains amidogene ($N.H_2$), being amidide of hydrogen, Ad.H. It has been also shown that the crystals of the body $H.I.+P.H_3$ are not cubes, but belong to a rhombic system. When I come to describe the compounds of mercury, I shall show that there exist similar bodies containing phosphuret of mercury and nitruret of mercury, and that the constitution of phosphuretted hydrogen may, with great reason, be supposed to be, not $P.H_3$, but that a quantity of phosphorus equal to one third of its ordinary atomic weight unites with an equivalent of hydrogen, its formula being $\frac{P}{3}.H.$, and the commonly received equivalent of phosphuretted hydrogen being in reality three equivalents, $=3.\frac{P}{3}.H.$ I therefore consider the compound which I have just described as having for its true constitution $H.I.+3\frac{P}{3}.H.$, as there will be hereafter described the bodies $Hg.Cl.+3.\frac{P}{3}.,Hg.$, and $2Hg.Cl.+3.\frac{N}{3}.Hg.$: the equivalent of nitrogen being capable of the same subdivision by three.

This *Hydriodate of Phosphuretted Hydrogen* is decomposed by water, hydriodic acid and phosphuretted hydrogen being given off, the last in the B variety. But if a little oxide of silver be sprinkled on the salt, the gas is evolved in its spontaneously inflammable condition. It burns when heated in air, but, in a dry tube containing no oxygen, it may be sublimed from place to place unaltered.

Chlorides of Iodine.—I have shown that chlorine and iodine unite in three proportions, forming bodies having the formulæ I.+Cl., I.+3Cl., and I.+5Cl. By much water the first and second are decomposed, producing muriatic and iodic acids, and iodine becoming free. The third, which was long ago discovered by Humphrey Davy, gives muriatic and iodic acids without separation of iodine. These bodies are interesting only as being employed to obtain the iodic and periodic acids, as already noticed.

Of Bromine.

This substance, which is intermediate in almost all chemical properties to chlorine and iodine, exists associated with those bodies in sea-water, in many varieties of sea-weeds, and in some of the brine-springs belonging to the deposites of rock-salt in the earth. In these cases it is generally combined with sodium or with magnesium, forming very soluble salts, which remain behind when the common salt crystallizes out by evaporation from sea-water. When a current of chlorine gas is passed through the mother liquor so obtained, which is called *bittern*, the bromine is set free, and tinges the solution yellow. On agitating this liquor with some ether, the bromine is completely taken up by it, and an ethereal solution of bromine, of a fine hyacinth-red colour, is produced; when this is acted on by potash, there is formed a mixture of bromide of potassium and bromate of potash, which by fusion gives off oxygen, and pure bromide of potassium remains; this is mixed with peroxide of manganese and sulphuric acid, and precisely as in the preparation of chlorine or of iodine, the bromine is set free and may be distilled over. It is necessary to condense the bromine with great care, and to receive it in water, to the bottom of which it sinks; the reaction that occurs is that $2S.O_3$, $Mn.O_2$, and K.Br. produce $(S.O_3 . Mn.O + K.O. . S.O_3)$ and Br.

Bromine is a liquid at ordinary temperatures, but at 4° it solidifies; it is deep red by transmitted, but black by reflected light; it is much heavier than water, its specific gravity being 2·97; its odour is like that of chlorine, but much more disagreeable, whence its name (from Βρωμος). It is very volatile, boiling at 116°; but even at common temperatures it forms copious fumes, which have the same orange-red colour as those of nitrous acid; the specific gravity of its vapour is 5·393; it does not conduct electricity; it must be preserved under water, as otherwise the quantity of vapour it would form might burst the vessel containing it. It dissolves sparingly in water, but copiously in alcohol and ether. A taper is extinguished by its vapour, but not immediately, burning for a moment with a green flame and much smoke. Some of the metals in fine powder or leaf burn spontaneously in its vapour, as in chlorine; a drop of liquid bromine, put in contact with a globule of potassium, unites with it explosively and with brilliant ignition. It bleaches vegetable colours, but leaves itself a yellowish stain, less intense than that of iodine; it is poisonous.

Bromine unites with water, forming a crystalline hydrate like that of chlorine.

With starch, bromine produces a fine yellow colour, which is not intense if the solution be very much diluted.

Bromine is easily recognised by the peculiar colour and odour of its vapour, which can only be confounded with that of nitrous and hyponitrous acid, from which its other characters completely separate it. A solution containing bromine or a metallic bromide gives, with nitrate of silver, a white, curdy precipitate, insoluble in nitric acid, but dissolved by ammonia. This precipitate is distinguished from the chloride of silver by giving vapours of bromine when heated with a little chlorine water

The equivalent numbers of bromine are 978·2 on the oxygen scale, and 78·4, hydrogen being unity.

Bromic Acid.—There is known only one compound of bromine and oxygen, the bromic acid, the history of which is still very imperfect. When bromine is dissolved in a solution of potash, bromide of potassium and bromate of potash are formed, 6Br. and 6K.O. giving 5K.Br. and $Br.O_5+K.O.$ On adding a solution of a salt of barytes to the liquor so obtained, bromate of barytes is precipitated, and this may be decomposed by sulphuric acid, which forms sulphate of barytes, leaving the bromic acid in solution.

The bromic acid has not been obtained solid; it is still more easily decomposed by deoxidizing agents than the chloric acid; thus the sulphurous acid and the phosphorous acid liberate bromine. The same effect is produced by sulphuretted hydrogen. Its salts have not been much examined, but appear to resemble the chlorates and iodates.

Its formula is $Br.O_5$, its composition by weight and equivalent numbers being,

Bromine, 66·18	One equivalent,	=978·2 or	78·40
Oxygen, 33·82	Five equivalents,	=500·0 or	40·00
100·00		1478·2	118·40

These elements are united by volume in the ratio of two volumes of bromine vapour to five volumes of oxygen.

Hydrobromic Acid.—The processes for obtaining the bromide of hydrogen are precisely the same as those described for preparing hydriodic acid in the liquid or in the gaseous form, to which I shall therefore refer (p. 315), bromine being substituted for iodine in every case. This gas is colourless; it is rapidly absorbed by water, the solution reacting acid; it is not decomposed by oxygen, nor does bromine decompose water, so that it stands between iodine and chlorine in that respect. It resembles muriatic acid in almost all its reactions, but is at once distinguished from it by evolving bromine on contact with chlorine or nitric acid. If bromide of potassium be acted on by oil of vitriol, the result is partly as occurs with a chloride, water being decomposed and hydrobromic acid evolved, and partly as occurs with an iodide, bromine and sulphurous acid being evolved together; hence hydrobromic acid cannot be prepared pure in that way.

The sp. gr. of hydrobromic acid gas is 2731, being produced by

One volume of bromine-vapour . . .	5393·0
One volume of hydrogen	68·8
united without condensation	5461·8
and hence one volume weighs	2730·9

The *Bromide of Sulphur* is a heavy reddish liquid, like chloride of sulphur, probably S_2Br.

There are two *Bromides of Phosphorus*, one liquid, $P.Br_3$, and the other solid, $P.Br_5$, which present complete analogy with the chlorides of phosphorus. Neither of these bodies presents particular interest.

The bromide of hydrogen unites with phosphuretted hydrogen, forming a compound similar to that already noticed, containing hydriodic acid. It is sufficient to mix the two gases together over mercury; a dense white cloud forms, which condenses on the sides of the glass in small crystals, which appear to be cubes, but are

not so really. This substance can also be formed in the indirect manner described for the iodine compound. It consists of an equivalent of each element, its formula being $H.Br.+P.H_3$, or, as I prefer to write it, for the reasons already stated, $H.Br.+3\,\frac{P}{3}.H$.

This body is volatile, and may be sublimed, provided neither oxygen nor water be present; heated in oxygen, it takes fire, and with water it is instantly decomposed.

The *Chloride of Bromine* and the *Bromides of Iodine* resemble in general characters the compounds of chlorine and iodine. The first, when decomposed by water, produces hydrochloric and bromic acids; the latter, on the contrary, gives hydrobromic and iodic acids. These bodies are not otherwise of interest.

Of Fluorine.

Although the existence of this body is rendered exceedingly probable by analogical reasoning, and recent experiments have gone very far in establishing its distinctive characters, yet it cannot be prepared in an isolated form, or exhibited like all the simple bodies as yet described; for such is the intensity and variety of its affinities, that no sooner is it liberated from combination with one substance, than it enters into union with some other, attacking the materials of which the apparatus used may be constructed. The most successful experiments made for examining it in its isolated form are due to two talented Irish chemists, the Messrs. Knox.

The only substances on which fluorine is incapable of acting being such as already are fully saturated with it, Messrs. Knox had vessels constructed of fluor spar (fluoride of calcium), which were filled with pure dry chlorine gas. Into these vessels was then introduced fluoride of mercury, and the whole carefully warmed. The chlorine decomposed the fluoride of mercury, forming chloride of mercury, and the fluorine was disengaged, Hg.F. and Cl. giving Hg.Cl. and F. There was in this way obtained a colourless gas, which acted with violence on the fragments of metallic foils, that by means of a very ingenious arrangement were submitted to its action. The small quantity of material on which the experiments were conducted did not allow of the metallic compounds so formed being analyzed; and the only doubt that can exist of the isolation of fluorine in this process is that, as it was liberated, it might have combined with the excess of chlorine present, and that the colourless gas may have been chloride of fluorine, and not the mere fluorine itself.

The specific gravity of gaseous fluorine, calculated from the analogy of its compounds to those of chlorine, is 1289; its equivalent number is 233·8, or 18.7.

Fluorine does not combine with oxygen.

The most important compound of fluorine that is known is the *Fluoride of Hydrogen*, or *Hydrofluoric Acid.* To prepare it, pure fluor spar, which consists of fluorine and calcium, is reduced to powder, and distilled in a leaden retort with twice its weight of the strongest oil of vitriol. The receiver must also be of lead, and be kept cool by ice. An acid liquor distils over, of an excessively suffocating odour, and so intensely corrosive, that a drop let fall upon the hand produces a sore very difficult to heal. This liquid is hydrofluoric acid, the reaction being that $H.O..S.O_3$ and Ca.F. give $Ca.O..S.O_3$ and H.F. Sulphate of lime remains in the retort.

The hydrofluoric acid, which is thus obtained in an anhydrous form, is very volatile, boiling at 60°. It is heavier than water, and becomes still more so when diluted to a certain degree. It dissolves the more oxidable metals rapidly with the escape of hydrogen gas, and the formation of a metallic fluoride. The only metals which it does not act upon are gold, platina, silver, and lead. There must be no solder about the leaden vessels in which the acid is kept, as it is acted on very violently. It is dangerous to have much to do with the anhydrous acid, from its corrosive power; and as a dilute acid answers for all practical purposes, a quantity of water is generally put into the receiver, into which the acid is distilled.

The most remarkable property of hydrofluoric acid is its action upon glass, which it corrodes and dissolves. The glass contains silica, which the hydrofluoric decomposes, $Si.O_3$ and $3H.F.$ producing $3H.O.$ and $Si.F_3$. This fluoride of silicon is a gas, decomposed by water in a way that will be soon described. Patterns or designs may therefore be etched upon glass by means of this hydrofluoric acid. There are two modes in which this operation may be conducted: 1st, by the liquid acid; 2d, by the acid in vapour. For the first, the glass plate being covered with a uniform coating of wax, the design is traced on it with the point of a needle or graving tool, taking care that the surface of the glass shall be laid bare throughout the whole extent of each line; a rim of wax being then formed round the edge of the plate, the liquid acid, the strength of which must be regulated by the depth of engraving required, is poured on the plate to the depth of two or three lines, and left for a time dependant on the judgment of the operator. When it has remained long enough, the remaining acid is poured off, and the wax cleared away. The etched portions of the glass are equally transparent with the others, and the design is therefore indistinct except in certain incidences of the light. A glass plate so prepared may be used as a copper plate to print from, but the risk of breaking is too great to allow of its introduction into practice.

To etch by the second mode, the plate of glass is prepared exactly as described for the first, except that there need not be any raised edge. A flat leaden basin, of the size of the plate, is used to hold the mixture of powdered fluor spar and oil of vitriol, and the glass plate is laid upon it, with the waxed side down; the basin is then heated so gently as not to melt the wax or injure the accuracy of the design; the hydrofluoric acid, which rises in vapour, acts upon the surface of glass exposed, and decomposes the silica, forming fluoride of silicon; but a sufficient quantity of watery vapour rises to decompose this substance, and a quantity of silica is regenerated and deposited upon the corroded surface, giving it a rough and white appearance, so as to be easily visible in every direction. When the action has continued long enough, the plate is removed from the basin, and the wax cleared off by means of some spirits of turpentine. Other uses of the hydrofluoric acid, such as in mineral analysis, will be described hereafter.

The composition and equivalent numbers of the hydrofluoric acid are as follows:

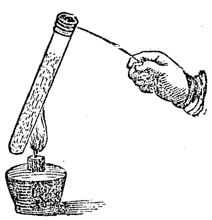
Fluorine,	94·93	One equivalent,	$=$233·8 or	18·7
Hydrogen,	5·07	One equivalent,	$=$ 12·5 or	1·0
	100·00		246·3	19·7

There are no other combinations known of fluorine with any of the simple bodies as yet described, except sulphur and phosphorus: these are dense volatile liquids. The *Fluoride of Phosphorus*, when decomposed by water, produces hydrofluoric acid and phosphorous acid; it is, therefore, $P.F_3$. When heated in the air, it burns, but the product of the combustion has not been examined.

Of Silicon.

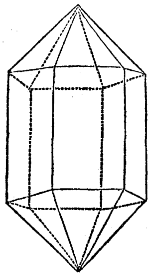
This substance is one of the most extensively distributed of the undecomposed bodies, constituting, probably, a sixth of the total weight of the mineral crust of the globe. It never exists free, but always in nature combined with oxygen, forming *silicic acid*, or, as it is termed in popular language, the earth *silica*. Quartz, in the state of rock and crystallized, flints, agate, sand, and many other mineral substances, are silica completely or nearly pure, and when combined with various metallic oxides, it forms the great family of silicates, which includes the majority of earthy minerals.

It is exceedingly difficult to deprive silicic acid of its oxygen; even by ignition with potassium it is but imperfectly decomposed. To prepare silicon, therefore, a somewhat complex body is selected to be acted on, the double fluoride of silicon and potassium ($2Si.F_3 + 3K.F.$), which is a white powder like starch, very sparingly soluble in water; a quantity of this substance is to be mixed with nearly its own weight of potassium, cut into little bits, and placed in an iron cylinder, or in a tube of hard glass, which may be held, as in the figure, over the flame of a spirit-lamp. As soon as the bottom of the tube has been heated to redness, vivid ignition occurs by the decomposition, which spreads, with little need of external heat, throughout the entire mass; when cool, the residual brown matter is to be washed carefully with water: fluoride of potassium dissolves, and the silicon remains behind; the $2Si.F_3 + 3K.F.$, acted on by $6K.$, give $9K.F.$ and $2Si.$ To have the silicon quite pure, numerous precautions are necessary, which need not be detailed here.



The silicon so obtained is a dull brown powder, which, when heated in air or in oxygen, takes fire and burns, forming silicic acid. If it be ignited in a closely covered vessel, it shrinks in volume, increases very much in density, and becomes insoluble in acids or alkalies, which, in its original form, it would dissolve in, with evolution of hydrogen gas; it then also cannot be made to burn in oxygen gas; it burns in the vapour of sulphur and in chlorine, combining with these bodies. When ignited with carbonate of potash, the silicon burns brilliantly, setting carbon free, and forming, with the oxygen of the carbonic acid, silicic acid, which combines with the potash. The equivalent number of silicon is 277·31 or 22·22, according as the oxygen or the hydrogen standard may be adopted.

Silicic Acid. Silica.—This, the only compound of silicon and oxygen, exists in nature completely pure, in masses constituting quartz rock, and in crystals which belong to the rhombohedral system; their ordinary form is represented in the margin.



It is exceedingly hard, and, in order to be reduced to powder, requires to be heated first to redness, and then thrown into a large mass of cold water. The piece of quartz cracks in every direction by being so suddenly cooled, and is then easily reduced to powder in an agate mortar. It may be obtained in a state of much more minute division, by melting, in a platinum crucible, a mixture of equal weights of carbonate of potash and of carbonate of soda, and adding thereto powdered flint, by small quantities at a time; the silica dissolves in the melted alkali, while carbonic acid gas is given off. When the alkaline silicates, so formed, are dissolved in water, and a stronger acid added, the silicic acid is precipitated as a gelatinous hydrate, which, when completely dried, forms a white powder, still somewhat gritty to the feel. When the gaseous fluoride of silicon comes into contact with water, a portion of it is decomposed, fluoride of hydrogen and silicic acid being produced; this last separates in the gelatinous form, but, on drying, becomes an exceedingly fine light powder.

Silica, even when prepared by precipitation, feels gritty between the teeth; when in mass, it is exceedingly hard, scratching glass and the generality of minerals. Its specific gravity is 2·66; it is fusible only by the oxyhydrogen blowpipe, in the flame of which it melts into a colourless glass; when once dried it is totally insoluble in water, but in its gelatinous form it is soluble to a small extent; hence many mineral waters contain silica, which, being gradually precipitated in the substance of decomposed organic matter, produces the silicious petrifactions in which the most delicate vegetable tissues are so beautifully preserved. The differences between silica in its dry and in its hydrated condition are so great, that we can scarcely suppose them to be satisfactorily accounted for by the presence of a substance for which the silica appears to have so little affinity. When a dilute alkaline solution of silica is decomposed by an acid, there is no precipitation, the silica remaining dissolved; but on evaporating the liquor to dryness, the silica assumes the insoluble condition, and remains behind when the saline constituent is dissolved. On the other hand, by the presence of an alkali, the insoluble silica is made to assume the soluble state.

There is some difference of opinion as to whether the compounds of silica and water are truly definite, but I look upon the existence of at least one, having the formula $2Si.O_3+H.O.$, as being certain; I have found the light spongy masses of silica deposited from volcanic springs, and on the edges of volcanic craters from Iceland and Teneriffe, to have accurately that constitution.

It is probable that a great deal of the silica which exists in nature has been originally deposited in the soluble condition. The structure of the agates, chalcedony, and many other minerals, proves that they were formed by a solution of silica having penetrated

into a cavity in the surrounding rock, and having then gradually dried down or crystallized. It is even pretty certain that the crystallized quartz is also of this aqueous origin.

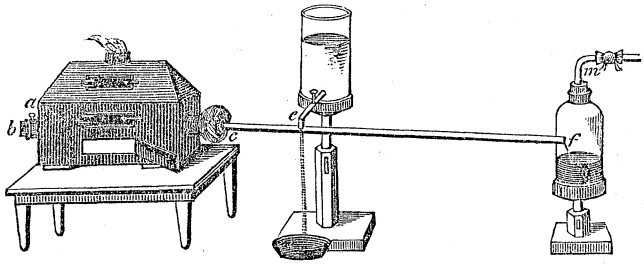
In the arts, silica is of exceeding importance, being an essential constituent of glass, porcelain, and every kind of delft and earthenware. For purely chemical purposes, it is only of interest from the compound which silicon forms with fluorine; the hydrofluoric acid being the only acid capable of dissolving silica.

The composition of silica and its equivalent numbers are as follows, its formula being $Si.O_3$.

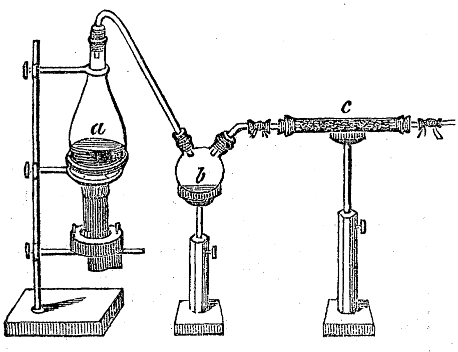
Silicon,	48·04	One equivalent,	=277·3	or 22·22
Oxygen,	51·96	Three equivalents,	=300·0	or 24·00
	100·00		577·3	46·22

Silicon does not combine with hydrogen nor with nitrogen: there exists a sulphuret of silicon, which is probably $Si.S_3$, as when acted on by water it produces soluble silica and sulphuretted hydrogen.

Chloride of Silicon.—This substance, although not itself important, is yet interesting from the fact that the method of preparing it is one by which a number of remarkable compounds of chlorine have been discovered, and hence it deserves to be described. Chlorine has no action on silica at any temperature; but if finely-divided silica be mixed with powdered charcoal, and heated to redness in a porcelain tube, *a*, *c*, inserted in the furnace, as in the figure, and by means of a glass tube at-



tached at *b*, a current of dry chlorine be made to stream over the ignited mixture, decomposition ensues, the oxygen of the silica combining with the carbon to form carbonic oxide gas, while the chlorine and silicon unite, producing the chloride of silicon, which, being a very volatile liquid, requires to be carefully condensed; for this purpose, the tube *c f* is wrapped up in a cloth, or a paper kept constantly wetted by a stream of water from the reservoir *e*, and the liquid produced then collects in the bottle *f*, while the oxide of carbon and the excess of chlorine pass off by the tube *m*. In this process the reaction is such, that 3Cl. acting on $Si.O_3$ and 3C., give rise to 3C.O. and $Si.Cl_3$.



The stream of dry chlorine may be very conveniently obtained by the apparatus here figured; the muriatic acid and peroxide of manganese are placed in the flask *a*, and the gas evolved, depositing the accompanying liquid in the receiver *b*, passes through the tube *c*, which, being filled with

fragments of recently-fused chloride of calcium, absorbs all the watery vapour The gas issues dry from the extremity, where it is connected with the end *b* of the porcelain tube in the preceding figure.

The chloride of silicon is a colourless liquid, denser than water; it boils at 124°; in contact with water, it is resolved into silica and hydrochloric acid, from whence its formula must be $Si.Cl_3$.

Fluoride of Silicon.—This is the most remarkable compound of silicon after silicic acid; it is a gas colourless and transparent; to prepare it, fluor spar and sand, or glass in powder, are mixed together, and heated in contact with oil of vitriol; the mass swells up very much, so that a large vessel must be employed. In this reaction we may look upon water as being decomposed or not, as the results may be explained in either way. Thus the oxygen of the silica may combine with the calcium, forming lime, and this with the sulphuric acid, while the silicon unites with the fluorine of the fluor spar. Or, water being decomposed, hydrofluoric acid and lime may be first produced, and the former, reacting on the silica, may reproduce water, and form fluoride of silicon. I prefer to omit here, as I did when describing the formation of chlorine, all the unnecessary theoretic agency of the water, and to express the decomposition as $3(S.O_3 . H.O.)$ with $Si.O_3$ and $3(Ca.F.)$ give $3(S.O_3 . Ca.O. . H.O.)$ and $Si.F_3$.

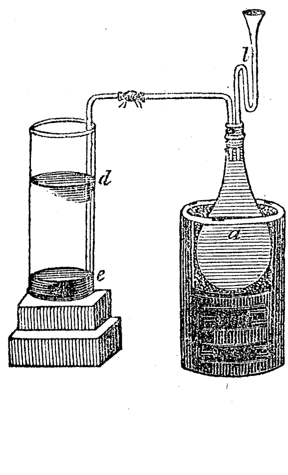
This gas must be collected over mercury, and in vessels dried with the greatest care. When it mixes with air, it forms dense white fumes, which arise from the formation of silica by the watery vapour present being decomposed.

It is colourless and transparent; its specific gravity is 3600. Its composition and equivalent numbers are as follows, its formula being $Si.F_3$.

Silicon,	28·32	One equivalent,	=277·3 or	22·22
Fluorine,	71·68	Three equivalents,	=701·4 or	56·22
	100·00		978·7	78·44

The hydrofluosilicic acid, or the double fluoride of hydrogen and silicon, cannot be obtained free from water, but its solution is of considerable importance as a chemical reagent, and hence its preparation requires to be described.

The mixture of powdered fluor spar and sand is introduced into the matrass *a*, which is imbedded in a sand-bath, as in the figure. By means of the siphon funnel *l*, the oil of vitriol is then poured in, and the gas evolved is conducted by the tube to the water in the vessel *d e*. If the tube opened into the water directly, so much silica would be deposited at its orifice as to stop it up every moment; and hence a quantity of mercury, *e*, is placed at the bottom, and the end of the tube dips into it. The gas bubble, therefore, does not touch the water until completely separated from the tube: it escapes from the surface of the mercury, and then it becomes invested with a



coating of silica, like a bag of tissue paper, of which many preserve their form for a certain time. The passage of the gas is to be continued until the water becomes thick from the quantity of silica separated; it is then to be poured on a fine linen cloth, and the silica removed by straining and pressure. In this process, one third of the fluoride of silicon is decomposed by the water forming silica and hydrofluoric acid, which last unites with the remaining fluoride of silicon to form the hydrofluosilicic acid, the formula of which is $2(Si.F_3)+3H.F$.

When a solution of this acid is heated, fluoride of silicon is given off, and hydrofluoric acid remains. Hence, although the hydrofluosilicic acid is without action upon glass, glass vessels in which it is evaporated are corroded.

The property of this acid which is of most interest to the chemist is, that it forms, by acting on the salts of potassium and barium, compounds, *fluosilicates*, or *double fluorides* of those metals which are very sparingly soluble in water; and hence it is used to detect the presence of these substances in solution. The precipitate so obtained is remarkable for being at first so gelatinous and transparent that it can be recognised in the liquor only by the play of colours in the light reflected from its upper surface. When collected on a filter and dried, these compounds appear like powdered starch. The constitution of the salts of the hydrofluosilicic acid resembles that of the acid itself, the hydrogen being replaced by a metal; thus the fluosilicate of potassium, already described as used for preparing silicon, is expressed by the formula $2Si.F_3+3K.F$.

The composition of hydrofluosilicic acid is easily known from that of the hydrofluoric acid and fluoride of silicon. Its equivalent number is 2696·4 or 216·2.

Of Boron.

The history of this substance presents a very close analogy with that of silicon. It was first obtained by decomposing boracic acid by galvanism, but is best prepared by acting on the fluoborate of potash by metallic potassium, exactly as has been described under the head of silicon. That salt consists of fluoride of boron united to fluoride of potassium; by the reaction, all the fluorine passes to the potassium, and the boron is set free.

Boron is a dark olive substance, which does not conduct electricity. It is insoluble in water and all other neutral fluids. When heated to 600° in the air or oxygen, it takes fire, and burning, forms boracic acid; the same effect is produced by boiling with nitric acid, or by ignition with nitrate or with carbonate of potash.

This element is not extensively distributed in nature, and only found combined with oxygen, forming boracic acid. This exists in certain springs in India, combined with soda, and, being crystallized in an imperfect way, was brought into commerce under the name of tinkal, or crude borax. The boracic acid is also found, and in much larger quantity, free, or combined only with a small quantity of ammonia, in the small volcanic lakes or lagoons of Tuscany. It accompanies the watery vapour which gushes out of fissures in the earth, and which contains also muriatic acid. The water of these

lakes is evaporated, and the boracic acid being crystallized, is imported into these countries for the manufacture of borax (borate of soda) and other salts.

The *boracic acid* is the only compound of boron and oxygen; it may be obtained quite pure from the native acid by boiling this with eight parts of water and a little white of egg, and filtering the solution. On cooling slowly, the boracic acid crystallizes in large brilliant plates, soft and unctuous to the feel, and of an irregular crystalline form. It may be also produced from borax by dissolving it in four times its weight of boiling water, and adding sulphuric acid until the liquor becomes sour to the taste. On cooling, the boracic acid crystallizes; but as it retains a little sulphuric acid and sulphate of soda, a second solution and crystallization is necessary to have it pure.

The crystals of boracic acid, so prepared, contain water, the oxygen of which is equal to the oxygen of the acid; when heated, this water passes off, and the acid melts; on cooling, it forms a colourless glass; when completely dry it is fixed, but in the presence of water it is carried off by the vapour in great quantity. The glacial acid, when exposed to the air, absorbs water, swells, and becomes opaque. The boracic acid is much more soluble in hot than in cold water, the crystals requiring twenty-six parts of water at 60°, and only three at 212° for their solution. Alcohol dissolves boracic acid copiously; and the solution, when set on fire, burns with a beautiful green flame, by which this body may easily be recognised. The boracic acid possesses but very feeble acid properties; many of its soluble salts possess alkaline reaction, and all are decomposed by the weakest acids. It does not redden litmus, but gives it a port-wine colour, and a strong solution of it browns turmeric paper like an alkali. At high temperatures, however, boracic acid may decompose the salts of the nitric, or even of the sulphuric acids, from the principles that have been already explained in the chapter on Affinity (p. 169).

The composition and equivalent numbers of boracic acid are as follows, its formula being $B.O_3$:

Boron,	31·22	One equivalent,	=136·2 or	10·9
Oxygen,	68·78	Three equivalents,	=300·0 or	24·0
	100·00		436·2	34·9

Boron does not combine with hydrogen or nitrogen; its compounds with sulphur and selenium are not important.

Chloride of Boron.—Boron burns spontaneously in chlorine gas, but the best way to prepare the compound of chlorine and boron is to proceed as described for making chloride of silicon, substituting boracic acid for the silica. The product is a gas, colourless and transparent, but producing dense white fumes in contact with damp air, owing to its decomposition, and the formation of boracic and hydrochloric acids. The presence of this last in the volcanic lagoons would render it probable that by some subterraneous action chloride of boron is generated, and is decomposed when mixed with the watery vapour simultaneously exhaled. The chloride of boron is rapidly absorbed and decomposed by water; its specific gravity is 4079; it contains $1\frac{1}{2}$ times its volume of chlorine; its formula is $B.Cl_3$.

Fluoride of Boron.—This substance is prepared in exactly the same way as fluoride of silicon, substituting the boracic acid for the silicic acid. It is a gas, rapidly absorbed and decomposed by

water, and generating hydrofluoboric acid, which is perfectly analogous to the hydrofluosilicic acid. It hence forms dense white fumes when mixed with damp air. Its specific gravity is 2362.

The hydrofluoboric acid is obtained by precisely the same plan as that described for the hydrofluosilicic acid. The boracic acid is deposited in crystals according as the gas is absorbed. If the liquor be evaporated without the acid deposited being removed, it is all again taken up and carried off as gaseous fluoride of boron. The liquid hydrofluoboric acid resembles, in the combinations that it forms, the hydrofluosilicic acid, and is similar to it also in constitution, its formula being $2(B.F_3)+3H.F$.

No other compound of boron of any interest is known.

The history of carbon involves so many considerations regarding the constitution and properties of organic substances, that I shall postpone entering upon it until after the description of the metals and their salts, and other compounds with the non-metallic bodies. I will then commence the study of the chemistry of organic substances with that of their most constant ingredient, carbon.

The compound of nitrogen with hydrogen (ammonia) has not been introduced among those of the non-metallic bodies with each other, because all the details of its history attach it to organic chemistry, under which head it will consequently be found. The hypothetical compounds of nitrogen and hydrogen (amidogene and ammonium) will be associated with it.

The substances hitherto described as chloride and iodide of nitrogen having been found to contain hydrogen, and to range themselves in an important series of organic combinations, have not been noticed in the chapter now closed, but will be found in their true position hereafter.

CHAPTER XII.*

OF THE GENERAL CHARACTERS OF THE METALS, AND OF THEIR COMPOUNDS WITH THE NON-METALLIC BODIES.

Although, as has been already noticed, the metals cannot be considered as forming a class of bodies, united by such analogies of chemical properties and laws of combination as would constitute a natural family, yet in their physical characters, and the most prominent facts of their technical history, they have so much in common as to render a notice of the conditions in which they exist in nature, the methods by which they are extracted upon the large scale, and the physical and chemical properties by which they are distinguished as a great division of the elementary bodies, necessary, before proceeding to the detailed history of the individual metals.

The metals are forty-two in number; their names have been already given in more than one place (p. 150 and 189). They reflect light powerfully, and hence possess what is termed metallic lustre. If the incident light be plane polarized, it undergoes a remarkable change, produced only by the metals and by diamond, becoming elliptically polarized on reflection. The metals are characterized very completely by their power of conducting heat and electricity, in which, although they differ among each other, yet the worst excels all non-metallic bodies. Lists of their relative conducting

powers in these respects have been already given (p. 92, 109, and 137). By the combination of these characters, the lustre and conducting power, the metallic or non-metallic nature of a body is always determined.

In the other properties of the metals there is found remarkable diversity; thus in colour, although silver is purely white, the majority of the metals are of various shades of bluish-white or gray, while copper and titanium are reddish coloured, and gold is yellow. In specific gravity, the metals include some of the lightest along with the heaviest solids that we know; the density of platinum being 21 times, of gold 19 times, and of potassium only $\frac{9}{10}$ that of water.

Some of the most important applications of the metals in the arts depend on their *malleability* and *ductility*. Those metals are malleable which admit of being rolled or beaten out into thin leaves; those being ductile which can be drawn into wire. Gold is the most malleable of metals; gold leaf may be obtained of $\frac{1}{282020}$ of an inch in thickness, and is hence the only metal in which any trace of transparency has been found; silver, copper, tin, rank next in malleability. The most malleable metals are not at all the most ductile; platinum, and even iron, can be obtained in finer wire than gold; platinum wire was made by Wollaston of $\frac{1}{30000}$ inch diameter; but a metal which is not malleable cannot be ductile, and *vice versa;* thus antimony, arsenic, and bismuth, the brittle metals, may be powdered in a mortar, but give neither leaves nor wire. The texture of the metals which produces the malleable and ductile conditions, depends closely upon temperature. Thus zinc is malleable and ductile at 300°; it loses this power, but remains tough, at 60°, while at 600° it becomes so brittle that it powders as easily as bismuth. In the drawing of lead pipe, and in making most of the metallic wires, there is a peculiar temperature required for the most perfect execution, by which is regulated the rapidity with which the process is carried on.

In strength and tenacity the metals differ also; iron is the strongest metal; an iron wire of a given thickness will support a greater weight than a similar wire of any other metal; copper is next to iron, but only about one half so strong; then platinum, silver, and gold: tin and lead are the weakest of the metals. The tenacity depends also on the molecular structure; if the wires had been annealed, so as to allow of an approach to internal crystallization, the tenacity is often found to be reduced to one half.

In their relations to heat the metals exhibit remarkable variety: but one metal is liquid at ordinary temperatures. All the metals are fusible, but they require for their liquefaction the greatest range of temperature which can be produced; thus mercury melts at —39°. potassium and sodium below the heat of boiling water; tin, lead zinc, antimony, and tellurium below a red heat, and many metals as platinum, are infusible in the most intense heat of a blast furnace and yield only to the flame of the oxyhydrogen blowpipe. In the history of each individual metal, its point of fusion will be given, so far as it is known.

The majority of the metals are fixed at the greatest heat of our furnaces; but mercury, zinc, cadmium, arsenic, tellurium, potassium, and sodium may be volatilized.

The generality of metals, when exposed to the air, particularly when damp, absorb oxygen and form oxides; some becoming merely tarnished upon the surface, others becoming thoroughly oxidized. Some metals, however, as gold, silver, platinum, palladium, and mercury, are not liable to this action. Those metals which oxidize when exposed to air, unite with oxygen at a higher temperature with great rapidity, many with actual combustion. Thus zinc, when heated to full redness, takes fire and burns brilliantly with a white flame, and the combustion of iron wire in oxygen is one of the prettiest lecture experiments. Mercury also, which does not tarnish when exposed to oxygen at common temperatures, becomes oxidized when heated to near its boiling point, but the oxide is resolved again at a red heat into oxygen and metallic mercury.

It is owing to their affinity for oxygen that many of the metals decompose water, and one of the most convenient classifications that have been proposed for ordinary use is founded on the fact of the different degrees of facility with which this decomposition proceeds. Thus,

Potassium, Sodium, Lithium, Barium, Strontium, Calcium, Magnesium,	The first class consists of metals which decompose water with lively effervescence, even at 32°.
Aluminum, Glucinum, Thorium, Yttrium, Zirconium, Lanthanum, Cerium, Manganese,	The second class consists of metals which do not decompose water with lively effervescence, except at about 212°, but very far below a red heat.
Iron, Nickel, Cobalt, Zinc, Cadmium, Tin, Chromium, Vanadium,	The third class consists of metals which do not decompose water except at a red heat, or at common temperatures in contact with strong acids.
Tungsten, Molybdenum, Osmium, Columbium, Titanium, Arsenic, Antimony, Tellurium, Uranium,	The fourth class consists of metals which decompose vapour of water energetically at a red heat, but which do not decompose it at common temperature, even in contact with strong acids.
Copper, Lead, Bismuth,	The fifth class consists of metals which decompose water at a red heat but very feebly, but whose oxides are not reducible to the metallic state by heat alone.
Silver, Mercury, Gold, Palladium, Platinum, Rhodium, Iridium,	The sixth class consists of metals whose oxides are decomposed alone at a high temperature, and which do not decompose water under any circumstances.

This kind of classification was first proposed by Thenard, and has been adopted by Graham in a form differing very slightly from that now given.

The following classification, although old, and founded solely on popular considerations, is yet so far consonant with the simplest characters of the metals as to be frequently referred to, and hence to be worthy of notice.

Those metals which do not tarnish on exposure to the air, and the oxides of which are reduced by heat alone, were termed the *noble* or *perfect metals;* at the head of this list stood gold, and at the bottom mercury.

All the other metals known to the older chemists were termed ordinary or *imperfect metals.* Of the metals of the first and second class, none had been then discovered; and of their oxides, only potash, soda, barytes, lime, magnesia, and alumina were known. From the old name of potash, *Kali*, with the Arabic prefix *al*, potash and soda, at one time confounded together, were termed *alkalies*, and ammonia, resembling them very much when dissolved in water or combined with acids, was also called an alkali; it was the volatile alkali, potash and soda being fixed alkalies; it was also termed the animal alkali, while soda was the mineral alkali, being derived from rock-salt or from the ocean; and potash received the name of the vegetable alkali, from its source being the ashes of plants growing upon land. The alkalies are characterized by being very soluble in water, and by neutralizing the strongest acids. They hence restore the blue colour of reddened litmus paper, and change the vegetable colours in general: the yellows to brown, the reds and blues to green.

Paper tinged yellow by turmeric is a delicate test of the presence of an alkali, by which it is browned.

Magnesia and alumina were termed *earths*, and silica was classed with them; these bodies, the *earths proper*, are insoluble in water, and have no action on turmeric paper.

Barytes, lime, and strontia were termed *alkaline earths;* they are soluble in water, but much less so than the alkalies; these solutions brown turmeric paper, and neutralize acids; but they are completely distinguished from the alkalies by their combinations with carbonic acid, which are insoluble in water, while the alkaline carbonates are very soluble in that liquid. These phrases of alkalies and earths are of constant recurrence in descriptions of chemical processes and results, and are thus seen to be founded on, and expressive of, some of the most important characters in those bodies.

Most of the metals combine with oxygen in more than one proportion, and the characters of the oxides are found to be regulated in a great degree by their composition. All protoxides (R.O.) (R. representing an equivalent of any metal) appear capable of combining with acids to form neutral salts; they constitute, properly, the metallic basis, but in many cases suboxides, (R_2O.), such as those of copper and mercury, form well-characterized salts, and sesquioxides, (R_2O_3), as those of iron, manganese, aluminum, and chrome, produce well-defined classes of salts also, which, however, in solution always possess an acid reaction. Peroxides, ($R.O_2$), as those

of manganese, tin, titanium, and lead, are either indifferent or feebly acid, and the higher degrees of oxidation lose all basic character, and become true acids, as the manganic acid, $Mn.O_3$, and the chromic acid ($Cr.O_3$).

The different oxides of the same metal frequently unite with each other, producing compounds which have great similarity to salts. Examples of this will be found under the heads of manganese, of iron, and of lead.

The affinity of the metals for chlorine is, in many cases, even more remarkable than that which they manifest for oxygen; thus gold and platinum, which resist even nitric acid, at once combine with chlorine; and tin, copper, mercury, antimony, arsenic, and bismuth, which require a high temperature to effect their rapid combination with oxygen, burn spontaneously when introduced into chlorine gas in a state of minute division. Most metallic oxides are decomposed by chlorine also at a high temperature; thus, if a stream of chlorine gas be passed over lime heated to redness in a porcelain tube, oxygen gas is expelled, and the calcium remains combined with chlorine. On this account, the chlorides are generally, after the oxides, the most important metallic compounds. Towards iodine, bromine, and fluorine, the metals are related nearly as to chlorine, the affinities being, however, much weaker towards bromine, and still more so towards iodine: of fluorine we do not as yet possess much positive knowledge, but its affinities appear to be at least as intense of those of chlorine.

The compounds of sulphur with the metals constitute a very extensive and important series, which, as has been more fully noticed in p. 284, resembles in a very striking manner the series of oxides of the same metal. Many metals, at a high temperature, combine with sulphur with brilliant combustion; and even at common temperatures, if iron filings and sulphur be mixed together with a little water, they will, in uniting, produce so much heat as to burst into flame, if the mass be moderately large. The metallic sulphurets, like the metallic oxides, are some acids and some bases, and these, by uniting, form the extensive classes of sulphur-salts. The metals combine with selenium and with phosphorus, subject to nearly the some conditions as in forming sulphurets, but the history of those compounds is not nearly so complete. As yet but very little has been done towards the history of the compounds of the metals with nitrogen, silicium, or boron.

Some of the metals, tellurium, arsenic, and antimony, combine with hydrogen, forming gaseous compounds, which resemble very closely the sulphurets and phosphurets of hydrogen in properties and constitution. In these bodies the hydrogen is the positive element, the metal playing the part of the sulphur or of oxygen.

The circumstances under which the metals are found in nature are exceedingly diverse. Some are found native, or only alloyed with other metals, as gold, silver, tellurium, bismuth, and some others. Many exist combined with arsenic, the sources of cobalt and nickel being almost exclusively their native arseniurets. Some metallic chlorides and iodides exist also native, but the most abundant forms in which the metals are to be found are combinations with

oxygen and sulphur. There are few of the metals that do not exist naturally in the state of oxides, which are either free or else combined with acids, forming salts. Thus lead, copper, iron, zinc, tin, manganese, antimony, are all found in abundance as native oxides, or as native sulphates, carbonates, arseniates, phosphates, silicates, &c. The majority of the metals exist also in nature combined with sulphur. The sulphurets of lead, of zinc, and of copper are the sources from whence the supplies of those metals are obtained; and the sulphuret of iron exists in great abundance, and, although not used for the extraction of the metal, is of great importance in the manufacture of green vitriol, of alum, and of sulphuric acid. These native compounds of the metals are termed *ores;* and the metal is said to be *mineralized* by the substance with which it is united.

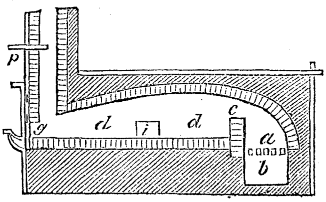
The processes followed in the extraction of the metals must be, of course, regulated by the composition of the ores in which it is contained; and as it will save the necessity of frequent repetition hereafter, I shall describe the general manner of treating each kind of ore, so far as may serve the purpose of an elementary work like the present, in which the introduction of minute and technical details would be useless and improper. In cases where the plan followed for any particular metal deviates essentially from that now about to be described, I shall notice the circumstance in its special history.

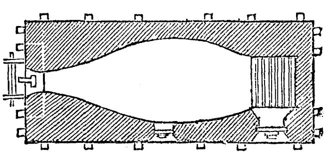
Where the metal exists in a simply oxidized condition, it is only necessary to heat the ore strongly in contact with the fuel, by which carbon is supplied in abundance for its reduction. The carbon combines with the oxygen, and the metal is set free. It is not often that the ores have this simple constitution, but in many cases the metal exists as a carbonate, and then the carbonic acid being expelled by the first application of the heat, the oxide which remains is reduced by the deoxidizing action of the ignited fuel. Thus the native carbonates of lead, of copper, of zinc, and especially of iron, are simply reduced in this way: the last mentioned is the ore which constitutes the great iron deposite of the neighbourhood of Glasgow.

If the mineralizing substance, however, be any other than oxygen, carbon, no matter how intensely heated, cannot produce any effect upon the ore. Thus the native sulphurets and arseniurets are not acted upon by carbon. Nor can the metals be obtained in a pure form from any of their salts, except the carbonates, by means of carbon, for the oxygen of the acid and base being simultaneously removed by its agency, the radical of the acid remains united with the metal, which is thus only changed into a new kind of ore. Thus, if sulphate of lead be heated with any of the forms of carbon, it is converted into sulphuret of lead, $S.O_3+Pb.O.$ and $4C.$ giving $S.+Pb$ and $4C.O.$ And if arseniate of iron be ignited with carbon, all the oxygen is removed, and the arsenic and iron remain in combination. In such cases, it is necessary to adopt somewhat more circuitous methods, suited to the constitution of the individual ores.

In the case of certain metallic sulphurets, the metal may be very simply separated by melting the ore with a proportional quantity of a metal having a greater affinity for sulphur. Thus metallic antimony is very generally obtained by the fusion of the native sulphuret with iron; Sb_2S_3 and $3Fe.$ giving $3Fe.S.$ and Sb_2. On the large

scale, however, this method would not be economically available. In order to extract the metal from its sulphuret, as in the generality of the ores of lead, of copper, and of zinc, the ore, first reduced to fine powder, is heated to redness in a current of air, by the oxygen of which the sulphur is converted into sulphurous and sulphuric acid, while the metal is oxidized. This process is termed *calcination.* A great part of the sulphuric acid formed is carried off with the current of air, and the remaining product is a sulphate of the metal, with excess of base. When the salt so formed is deoxidized by contact with the ignited fuel, the excess of oxide abandoning its oxygen, yields an equivalent quantity of metal, which, however, would be impure and of inferior quality, by having dissolved a portion of the sulphuret reproduced by the reduction of the sulphur from the sulphuric acid. It is therefore necessary to get rid of that residual portion of the sulphuric acid before the deoxidizing process commences, and this is effected by mixing up a proper quantity of lime with the calcined mass. The lime decomposes the metallic sulphate, combines with the sulphuric acid, and sets the oxide free; and when the deoxidizing flames of the furnace pass over the calcined mass, the metallic oxide being reduced, yields a pure metal, while the sulphate of lime, by losing its oxygen, is brought to the state of sulphuret of calcium, and remains as glassy scoria upon the surface without injury. This kind of operation is generally carried on in a sort of furnace termed *reverberatory,* from its office of beating down the flames from the fireplace upon the materials strewed upon its hearth. The adjoining figures will give an idea of its construction. The upper is a vertical, and the lower a horizontal section, to which the same letters apply. *a* is the fireplace, and *b* the ash-pit; at *c* a low wall is raised, termed the *bridge*, and the flames and heated air ascending from the fire are reflected downward by the low, vaulted roof, and, impinging upon the *hearth*, or sole of the furnace, *d*, produce the greatest heating effect upon the materials laid thereon. The openings *i* and *g* serve for the introduction of the materials, and for giving them the arrangement, agitation, and mixture most conducive to the success of the operation. The damper, *p*, in the flue, regulates the draught, and hence the intensity of the fire.





In this furnace, the calcining or oxidizing, and the reducing or deoxidizing effect is produced, according as the supply of fuel and of air is regulated; and thus the two stages just described, in the extraction of a metal from its native sulphuret, are carried on. The hearth, *d*, is generally dished or concave towards the centre, so that the reduced metal, in its melted condition, may flow there, and be run out by an aperture in the side of the furnace when the operation is concluded.

In the case of sulphuret of lead, a very simple and beautiful pro

cess of reduction consists in roasting the ore at a moderate temperature, so that about one half of it shall be converted into sulphate of lead by oxidizement, without any of the sulphuric acid being driven off; and then, having mixed this up well with the unaltered portion of the ore, increasing the temperature very rapidly, so that the two shall be fluxed together. The result is the complete conversion of the mixture into sulphurous acid gas, which passes off, and pure metallic lead, which remains, the sulphur of the unaltered ore combining with the sulphur and oxygen of that portion which had been oxidized. Thus $S.O_3+Pb.O.$ and $S.+Pb.$ produce exactly $2S.O_2$ and $2Pb.$

One of the most interesting processes of reduction is that by which iron is obtained from its most abundant ore, the clay iron stone. This substance consists of oxide of iron of greater or less purity, combined with alumina and silica. Now, as carbon cannot deprive silica of oxygen except under very peculiar circumstances, such as those described in page 323, so the metal cannot be obtained by mere deoxidation; and even if the oxygen were removed, the result would not be pure iron, but a compound of silicon and iron, which, indeed, is formed in small quantity, and is found generally in cast iron. It is necessary, therefore, to decompose the silicate of iron of which the ore is constituted, and this is effected by means of lime. The coal or coke and the ore are introduced into the furnace, mixed with a proportion of limestone, which, being calcined by the heat, yields lime, which seizes upon the silicic acid, and the oxide of iron being set free, is immediately reduced by the carbon of the fuel with which it is in contact, and produces metallic iron. The lime, the silica, and the alumina being melted together, form a substance of a nature somewhat between glass and porcelain, which floats upon the mass of melted metal, and constitutes the slags or *scoriæ* of the iron furnaces.

In the case of ores containing arsenic, of which only the arseniurets of cobalt and nickel are of technical importance, the method followed is to roast the ore in a furnace so constructed that a powerful oxidizing action shall be produced by a current of air streaming over the ignited ore; both metals being thus oxidized, arsenious acid, and oxide of cobalt or of nickel are produced; the greater part of the former is expelled by the heat, and, being carried off by the draught, is conducted into large chambers, where it is gradually deposited under the form of a fine white powder upon the walls and floor. The metal with which the arsenic had been combined remains in the state of oxide united with a little arsenious acid, and is subsequently extracted or employed in other processes.

The reduction of a metal from the state of sulphuret is frequently effected upon the small scale by fusion with a mixture of lime and charcoal, or of carbonate of potash and charcoal, which last is familiarly termed *black flux*. The theory of this process is very simple. Thus, if sulphuret of antimony, lime, and charcoal be melted together, the sulphur combines with the calcium of the lime, the oxygen of which unites with the antimony, Sb_2S_3 and $3Ca.O.$ giving $3Ca.S.$ and Sb_2O_3. This last is then decomposed by the charcoal, the oxygen combining with the carbon, and the metallic antimony separates.

The black flux used in such operations is prepared by deflagrating together equal parts of nitre and cream of tartar; the nitrogen and oxygen of the former unite with the carbon and hydrogen of the latter, forming carbonic acid, nitrogen, and water: the potash of both remains behind as carbonate, mixed with the excess of carbon which had escaped combustion. If two parts of nitre be used with one of cream of tartar, there remains after deflagration a white mass of carbonate of potash, which is known as *white flux*, and used in processes where the deoxidizing effect of the carbon is not required. Thus, for the reduction of chloride of silver, it is sufficient to fuse it with half its weight of white flux; the chlorine combines with the potassium, and the silver, which at a lower temperature would have united with the oxygen and carbonic acid, is separated, those two bodies escaping in the gaseous form; the formula of the reaction being that K.O. . $C.O_2$ and Cl.Ag. give K.Cl. and free Ag., while O. and $C.O_2$ are driven off.

Hydrogen, although inapplicable to the reduction of the metals upon the large scale, and for the purposes of the arts, is yet to the chemist a most valuable agent for this office, as it acts upon all varieties of metallic combinations, whether oxides, chlorides, or sulphurets; and that the results it gives are so accurate as to serve as bases for some of the most fundamental propositions of the science. Thus we have already seen that the composition of water is best determined by the action of hydrogen gas upon oxide of copper, and in analytical investigations, the isolation of a metal, by decomposing its chloride or sulphuret in a stream of hydrogen gas, is frequently employed. The deoxidizing action of hydrogen is occasionally used in an indirect manner. Thus a very convenient mode of obtaining silver from the chloride consists in fusing it with some common resin: this consists of carbon, hydrogen, and oxygen, of which only the hydrogen is active; it combining with the chlorine carries it off as muriatic acid gas, while the metallic silver is separated. If the chloride of silver be diffused through water rendered slightly acid, and a slip of zinc be introduced, an evolution of hydrogen commences, and the silver separates as a fine metallic powder as the zinc dissolves. But the action is here more properly galvanic; an equivalent (32·3) of zinc combining with the chlorine in place of each equivalent (108) of silver which is set free. The precipitation of copper from the water of copper mines, which holds sulphate of copper dissolved, by dipping therein pieces of iron, and, indeed, all cases of the precipitation of one metal by another, are referrible to the same source.

The physical agent, electricity, which has been already found to influence chemical action to so remarkable a degree, has been employed with considerable success in the reduction of certain metals. It was first applied by Davy, who thereby made his wonderful discoveries of the composition of the alkalies and earths. It has been totally superseded in that point of view by simpler processes, but has recently been applied by Becquerel, upon the large scale, to the extraction of the precious metals from their ores.

There are many other methods of reduction, which, however, being limited in their application to individual metals, will form more properly a part of their special history.

CHAPTER XIII.

OF THE INDIVIDUAL METALS, AND OF THEIR COMPOUNDS WITH OXYGEN, SULPHUR, SELENIUM, AND PHOSPHORUS.

SECTION I.

METALS OF THE FIRST CLASS.

Of Potassium.

POTASSIUM is the metallic basis of the alkali potash. It was originally discovered by Sir Humphrey Davy, who obtained it by submitting a piece of caustic potash, slightly moistened, so as to be a conductor of electricity, to the action of a powerful galvanic battery; the water and the potash were simultaneously decomposed, oxygen being evolved at the positive electrode, while hydrogen and potassium were separated at the negative wire. From the heat generated by the intense power used, the metallic globules generally burned as soon as they came into contact with the air, and it was with difficulty that a quantity was obtained sufficient for the important researches in which it was employed by its illustrious discoverer. By using mercury as the negative electrode, the decomposition can be effected by a much weaker force, and even with a single pair of plates, as in the arrangement of Dr. Bird, described in p. 199.

The decomposition of potash by truly chemical means is due to Gay Lussac, but it is by the process of Brunner that the metal is now universally obtained. As it is carried on only, however, in the most extensive and best-appointed laboratories, a very short sketch of it will suffice here.

Cream of tartar, which consists of tartaric acid united to potash, is to be ignited in a covered crucible, until there remains a mass of carbonate of potash mixed with carbon in a state of very minute division, and this mass is to be intimately mixed, while still hot, with a quantity of coarsely-powdered wood charcoal, which serves to render the whole porous, so as to allow of the escape of the gases generated in its interior without its swelling up. The material so prepared is introduced into an iron bottle, such as those in which quicksilver is imported; to the mouth of the bottle, which is laid horizontally in a wind furnace, is adapted a short iron tube, passing to a copper condenser partly filled with rectified naptha, and so constructed with partitions as to exclude the air, while there passes through it a stout iron wire, terminated by a screw, with which the iron tube can be cleared of any solid material that might be deposited in it. The apparatus being so arranged, and the receiver surrounded by ice, a fire is lighted in the furnace, and when the iron bottle has become white hot, the decomposition of the potash begins, the metal distils over, and condenses in the receiver

in globules, which are protected by the naptha, in which they sink, while the oxygen of the potash and of the carbonic acid combines with carbon, forming carbonic acid, which, escaping under the partitions in the receiver, passes away; $K.O.+C.O_2$ and 2C. producing K. and 3C.O. The great difficulty and loss in this process arise, however, from a cause which is not at first apparent; it is, that carbonic oxide and potassium unite to form a dark gray mass, which sublimes, and, condensing in the short iron tube, renders the screw necessary to keep the passage clear, and frequently causes the failure of the process. Even in the most successful results, one half of the metal actually reduced is lost by combining with the carbonic oxide.

The potassium thus obtained is very impure, containing much carbon, and a quantity of that compound of carbonic oxide which passes over into the receiver. To purify it, it is redistilled in cast iron retorts, from which the air has been previously excluded by vapour of naptha, and it is thus obtained in globules like peas, in which state it may be preserved under naptha perfectly free from oxygen.

At common temperatures, potassium is soft, and may be moulded in the fingers like wax. At 32° it is quite brittle, and crystallizes in cubes; at 70° it is pasty, and at 150° perfectly liquid. At a dull red heat it boils, forming a green vapour, and may, as described above, be easily distilled. It is specifically lighter than water, its specific gravity being 0·865.

The colour of potassium is of a bluish white, but its surface instantly becomes gray when exposed to the air, owing to the absorption of oxygen and the formation of a crust of potash. If it be heated, it burns with a vivid violet flame. So great is its affinity for oxygen that it decomposes water, and even ice, with great violence, so much heat being evolved that, if the experiment be made in the air, the hydrogen gas evolved and the metal both inflame and burn with a fine violet colour. When the metal has been all consumed, a globule of fused dry potash remains, which, when it has cooled to a certain degree, combines with water with a loud report, and instantly then dissolves.

Potassium is remarkably characterized by its great affinity for oxygen, which it abstracts from almost all bodies; thus its use in the preparation of boron and silicon has been already noticed; and although, at very high temperatures, iron and carbon take oxygen from potassium, yet at a lower degree of heat, oxide of iron and carbonic acid are both decomposed by potassium, carbon being deposited from the one, and metallic iron separated from the other.

The symbol of potassium is K., the initial of the word Kalium, by which the metal is designated by most of the Continental chemists; the old name kali being still retained in preference to the word potash, which has been adopted only in Great Britain and in France. The equivalent is 490 or 39·3, according to the scale.

Oxides of Potassium.—Potassium combines with oxygen in two proportions, forming a protoxide K.O., and a peroxide $K\,O_3$.

The protoxide of potassium constitutes the important alkali *potash;* it can only be obtained free from water by exposing potassium

to the action of dry air, when it is converted into a white powder, which is fusible at a red, and volatile at a white heat; if this substance be once united with water, it cannot be separated from it except by combination with an acid. The potash of commerce, and that used in the laboratory, is, therefore, always hydrate of potash; the dry potash, in uniting with water, becomes ignited. Before the discovery of carbonic acid, the alkalies and their carbonates were distinguished from each other by the epithets of mild and caustic, and hence for medicinal purposes, and in some pharmacopœias, the hydrate of potash is still termed caustic potash.

To prepare a solution of potash, the carbonate of potash of commerce, derived from the sources to be detailed in its description, is to be dissolved in ten parts of water, and the solution being made to boil smartly, is to be decomposed by one part of slacked lime in fine powder, which is to be gradually added, the boiling being briskly kept up; the lime abstracts the carbonic acid from the potash, and carbonate of lime is formed, which at that temperature, constituting minute crystals of arragonite, is rapidly and completely deposited. The clear liquor is to be tested occasionally by adding to a small quantity of it an excess of muriatic acid; as soon as the absence of effervescence shows that all the alkaline carbonate has been decomposed, the pan is to be removed, and being laid aside, carefully covered, until the carbonate of lime has been well settled, the clear liquor may be siphoned off. The decomposition of the carbonate of potash by the lime would take place also at ordinary temperatures, but the precipitate would be in the rhombohedral form, and being specifically lighter and more finely divided, would occupy much more room, and would not separate so well. If the carbonate of potash be dissolved in less than six parts of water, it is not decomposed by lime; on the contrary, when a strong solution of caustic potash is boiled with carbonate of lime, carbonate of potash is produced, and lime set free.

When the solution of caustic potash is evaporated in a basin of iron, or silver, or platina, there remains a liquid which solidifies on cooling into the *hydrate of potash*, K.O. . H.O. This liquid is generally run into cylindrical moulds, in which form the caustic potash or fused potash of the shops is generally found. In this state it is, however, impure, and it requires to be freed from the admixed sulphate and carbonate of potash, chloride and peroxide of potassium, and oxide of iron, which it generally contains, by being dissolved in absolute alcohol, the solution evaporated to dryness, and the remaining potash fused a second time.

Hydrate of potash is a pure white solid, of a crystalline fracture; it fuses below redness. In the fingers it has a peculiar soapy feel, owing to its dissolving the cuticle, with which it forms a kind of soap; it acts powerfully on all organic tissues, dissolving and decomposing them, and hence its use in surgery, and its name of caustic potash. It dissolves in water, with the evolution of considerable heat; a concentrated solution of it crystallizes when exposed to cold, in rhombic octohedrons, whose composition is K.O.+5H.O.

The solution of potash is pre-eminently alkaline; it neutralizes the strongest acids, browns turmeric paper, and restores the blue colour

of litmus paper reddened by an acid. It absorbs carbonic acid rapidly from the air, and must hence be preserved in close vessels. It acts rapidly on glass containing much alkali or lead, and hence should be preserved in bottles of common green glass.

The uses of potash in chemistry are too numerous to mention; it being the strongest base, is employed in almost all cases of saline decomposition, and its various compounds are of great importance in the chemical arts, of which many will be noticed hereafter in detail.

Potash is distinguished, when free, first, by its general alkaline characters, and by its not being precipitated by carbonate of soda, which separates it from everything but soda and ammonia. From the latter it is known by the brown stain produced on turmeric paper being permanent, whereas the brown colour produced by ammonia disappears when the paper is warmed; and from soda it is known by giving with an excess of the perchloric, tartaric, and hydrofluosilicic acids, sparingly soluble salts, whereas the soda salts of these acids are all easily soluble. A solution of potash, if neutralized by muriatic acid, gives, on the addition of chloride of platinum, a fine yellow precipitate, whereas, with a solution of soda, no precipitation occurs.

The salts of potash act in all respects similarly, except that, as there is no alkali in excess, the action on vegetable colours is not that of an alkali. The salts of ammonia resemble precisely the salts of potash in their action on those precipitants described above, but they are at once distinguished by the application of heat. The salts of ammonia are all volatilized, either with or without decomposition, by a red heat, while those of potash are fixed, and give to the flame of the blowpipe a distinct and characteristic violet tinge.

Potash consisting of an equivalent of each element, its formula is K.O., and its composition,

Potassium,	83·05	One equivalent	=490 or	39·3
Oxygen,	16·95	One equivalent	=100 or	8·0
	100·00		590	47·3

Peroxide of Potassium. K.O_3.—This substance, which is of very little importance, is formed by burning potassium in an excess of oxygen gas; it is a yellow powder, decomposed by water, potash dissolving, and oxygen being given off. When hydrate of potash is heated to redness in air, some peroxide is always formed, and hence the fused potash of the shops generally gives off minute bubbles of oxygen gas when dissolved in water.

Sulphurets of Potassium.—When potassium is gently heated in contact with sulphur, they unite with brilliant combustion, and, according to the proportions in which they are employed, form the sulphurets of potassium, of which there are altogether four. These bodies are, however, always prepared in practice by more economical processes.

If sulphate of potash be ignited in a glass tube, and a current of dry hydrogen gas be passed over it, all the oxygen, both of acid and base, is removed in the state of water, and *protosulphuret of potassium* remains. Thus K.O. . S.O_3 and 4H. produce 4H O. and K.S. The same result follows from igniting strongly, in a crucible, a mixture of charcoal and sulphate of potash; all the oxygen is removed as carbonic oxide, and the sulphur and the potassium remain in combination, K.O. . S.O_3 and 4C. giving 4C.O. and K.S.

This protosulphuret is of a brown colour, fusible below a red heat, easily soluble, and its solution is yellow, and reacts highly alkaline and caustic. When exposed to the air, it absorbs oxygen rapidly; and in preparing it from sulphate of potash, by carbon, if lampblack be used, so that the product shall be in a state of very minute division, it takes fire spontaneously on coming into contact with the air, constituting a *pyrophorus*. If the protosulphuret of potassium be acted upon by acids, water is decomposed, K.S. and H.O. giving K.O. and H.S.; the potash remains united with the acid, and the sulphuret of hydrogen is given off. No solid sulphur is deposited, and the liquor remains clear.

A solution of the protosulphuret dissolves sulphur in large quantity, the higher sulphurets being formed. It absorbs sulphuretted hydrogen in such proportion that a compound is produced, K.S.+H.S., exactly similar to the hydrate of potash, K.O.+H.O.

The *tersulphuret of potassium* corresponds to the peroxide, its formula being $K.S_3$. It constitutes the mass of the *hepar sulphuris*, liver of sulphur, of the pharmacopœias. It may be prepared by fusing, at a low red heat, one part of sulphur and two of carbonate of potash, the mass being kept liquid as long as it effervesces, from carbonic acid gas being evolved. In this reaction, a quantity of oxygen from the potash combines with one portion of the sulphur, forming hyposulphurous or sulphuric acid, according to the temperature, while the remainder of the sulphur combines with the potassium, producing a sulphuret, the composition of which is determined by the quantity of sulphur present. With the above proportions the reaction may be considered thus: $4(K.O.+C.O_2)$ and 10S. give $3K.S_3$ and $K.O.\,.\,S.O_3$, which constitute the fused mass, while $4C.O_2$ is driven off with effervescence. If, however, equal weights of carbonate of potash and of sulphur be employed, the sulphuret formed contains five equivalents of sulphur: it is the pentasulphuret.

These sulphurets resemble each other completely in external appearance; they are liver-brown; they deliquesce in the air, and absorb oxygen rapidly. Their solutions, which are at first deep yellow, become colourless by uniting with oxygen, hyposulphite of potash being formed, and sulphur precipitated. If a solution of the tersulphuret or pentasulphuret be treated with an acid, water is decomposed, and potash being formed, sulphuret of hydrogen is produced; the remaining sulphur then separates in a state of very minute division, and of a milk-white colour, constituting the *lac sulphuris*, or the *sulphur precipitatum* of pharmacy. If the acid employed be strong and in great excess, a quantity of bisulphuret of hydrogen is formed, as explained in page 293.

Rose is of opinion that the whiteness of precipitated sulphur depends not merely upon its minute division, but that it is owing to the presence of a trace of bisulphuret of hydrogen. When the *hepar sulphuris* is decomposed by an acid, it is not merely that the excess of sulphur is set free, but in addition, as there is always hyposulphurous acid present; this, when evolved, acts on the sulphuretted hydrogen, and the sulphur of both is precipitated, water being formed; $S.O_2$ and 2H.S. giving 2H.O. and 2S.

The *Pentasulphuret of Potassium* is prepared perfectly pure by decomposing sulphate of potash by sulphuret of hydrogen, at a red heat. Thus $K.O.\,.\,S.O_3$ and 4H.S. give $K.S_5$ and 4H.O. This reaction supports very much the view that this pentasulphuret is really sulphate of potash, in which the oxygen, both of acid and base, is replaced by sulphur, for $K.S_5$ may be constituted of K.S. and $S.S_3$.

The seleniurets of potassium are similar in constitution to the sulphurets. They evolve seleniuret of hydrogen when treated by acids, with precipitation of selenium when it is present in greater proportion than one equivalent.

Of Sodium.

Sodium exists in great quantities in the mineral kingdom, especially combined with chlorine, as common salt, of which enormous deposites are found in England, Poland, and elsewhere, besides forming the leading saline ingredient of the waters of salt lakes and of the ocean. It is found in many minerals, and is remarkably prevalent in the animal fluids, all of which contain common salt. It is, indeed, from the chloride of sodium that we derive, whether directly or indirectly, all the supplies of the various compounds of this metal.

The discovery of sodium was made in the same manner, and im mediately subsequent to that of potassium, by Humphrey Davy, and it is now prepared in exactly the same manner as that metal. It is, however, much more easily prepared; its reduction does not require so high a temperature, and it does not unite with carbonic oxide, so that the formation of the black sublimate, which is the principal source of loss and failure in preparing potassium, does not occur.

Sodium is lighter than water, its sp. gr. being 0·972; it consequently floats upon that liquid; and when a globule of the metal is thrown into a basin of water, this is decomposed with great rapidity, hydrogen being evolved; but the action is not so energetic as with potassium; the gas does not take fire spontaneously. But if the globule be prevented from moving about, the water becomes heated, and the action increases so much as to set fire to the gas; this occurs when there is so little water that the globule does not swim, or when it is fastened to the edge of the vessel, or if the water be thickened by gum or starch. If some oil of vitriol be added to the water, the action is so much more active, that combustion occurs even when the metallic globule moves rapidly about.

The symbol of sodium is Na., derived from the word Natrium, as soda still retains in many countries the name Natron. Its equivalent numbers are 291 or 23·3.

Sodium unites with oxygen in two proportions, forming the protoxide, or soda, Na.O., and the peroxide, of which the constitution is not exactly known. This last is prepared just as the peroxide of potassium, which it resembles completely in its properties. The former only requires detailed notice.

The preparation of dry soda is effected like that of potash, by heating the metal in dry air or oxygen. It is grayish white, and absorbs water with excessive power. From the hydrate of soda the water can be expelled only by an acid. The caustic soda is, therefore, always like caustic potash, a hydrate of the alkali. For the preparation of caustic soda, the same process is to be followed as for that of potash. The carbonate of soda of commerce, dissolved in boiling water, is decomposed by slacked lime, it being necessary, however, to use one third more lime, from the smaller equivalent number of soda. The solution of caustic soda resembles that of caustic potash in all its alkaline characters, but its action is not so intense. It is a weaker alkali, its salts being decomposed in all cases by potash.

The soda consists of an equivalent of each element; its formula is Na.O., and its composition,

Sodium,	74·42	One equivalent	=291 or	23·3
Oxygen,	25·58	One equivalent	=100 or	8.0
	100·00		391	31·3

The detection of soda is very simple. On adding to a solution of the substance to be examined a solution of carbonate of soda, if there be no precipitate produced, the base of the salt present must be an alkali. On then applying the various tests for potash and for ammonia detailed in the last section, if no evidence of their presence

be obtained, the alkali must be soda; and even where potash also is present, a small quantity of soda may be recognised, by its tinging the flame of the blowpipe of a fine yellow colour.

The compounds of soda are very numerous and important, and will be described in their proper place, among the salts.

The sulphurets of sodium resemble so completely the sulphurets of potassium as not to require more than a reference to their description. To the seleniurets of sodium the same remark applies.

Lithium.

This metal is found only in a few minerals, of which one of the most common, spodumene, occurs at Killiney, near Dublin. This mineral is a double silicate of the alkali lithia (oxide of lithium) and alumina. The metal has been obtained by voltaic decomposition, but only in very small quantity. It is white, like sodium, and becomes oxidized immediately on exposure to the air. Its symbol is L., and its equivalent number 80·3 or 6·4.

To obtain lithia, the simplest process is to mix the mineral containing it (generally lepidolite or spodumene), previously reduced to very fine powder, with fluor spar, and digest the mass with oil of vitriol, until it is completely decomposed; the silica is carried off by the hydrofluoric acid (see page 324), and the lime, the alumina, and the lithia remain combined with the sulphuric acid. By the action of a small quantity of water, the sulphates of lithia and alumina are dissolved out, and the last then precipitated by ammonia. The sulphates of lithia and ammonia being then ignited, the sulphate of ammonia is decomposed, and the sulphate of lithia obtained pure. This is but a general outline of the process, which requires many additional operations for a fully successful result.

Lithia is distinguished from the other alkalies by the sparing solubility of its carbonate, in which character it approximates to the property of the earths, thus connecting the two classes of metals. Being so rarely found, and of no application in the arts, its history is not of much importance.

Lithia is recognised by the sparing solubility of its carbonate, and by tinging the flame of the blowpipe of a brilliant red colour. This last character easily distinguishes it from soda. Lithia is a protoxide, its formula being L.O.; its equivalents 180·3 or 14·4.

The sulphurets and seleniurets of lithium do not possess any interest.

The alkali ammonia might, on one hypothesis of its nature, be described here. When combined with hydrogen, it is considered by Berzelius and many other chemists to form a remarkable compound metal, *ammonium*, $N.H_4$, whose relations to potassium are of an exceedingly intimate kind; and the salts of ammonia, which contain ammonia and water, $N.H_3+H.O.$, are looked upon as consisting of an oxide of that metal, $N.H_4.O.$ in combination with an acid. I prefer, however, to study the history of ammonia, and all the classes of compounds into which it enters, among the bodies of organic origin.

Barium.

Barium is found exclusively in the mineral kingdom, where its oxide, barytes, is the basis of several minerals, as the sulphate and carbonate, which are the usual sources from which it is obtained for use.

The metal barium was discovered by Sir Humphrey Davy immediately after the discovery of the basis of the alkalies. It may be prepared by voltaic action, as described under the head of potassium,

or much better by passing the vapour of potassium over barytes heated to redness; the potassium takes the oxygen of the barytes, and the barium is set free. By washing the residue with mercury, the metallic barium is dissolved out, and the mercury being then distilled off in a retort of hard glass, the barium remains behind; it is a white metal like silver; it fuses below a red heat; it is denser than oil of vitriol: it decomposes water with great rapidity, evolving hydrogen gas and forming barytes (oxide of barium).

The name barium is derived from βαρυς, heavy; the native sulphate of barytes having been called formerly *terra ponderosa*, or *heavy spar*. Its symbol is Ba.; its equivalent numbers 856·9 or 68·7.

Barium combines with oxygen in two proportions, forming a protoxide, which is the earth barytes, Ba.O., and a deutoxide, $Ba.O_2$. The preparation of this last has been described so fully when explaining its only important use, the formation of deutoxide of hydrogen (p. 258), that it need not be farther noticed here. The protoxide, barytes, is, however, one of the most important earths.

To procure pure barytes, the nitrate of barytes is to be gently heated to redness in a porcelain crucible. It fuses at a dull red, and boils briskly from the rapid escape of oxygen; when this has terminated, there remains a gray loosely coherent powder, which is barytes. The melted salt is in this process very apt to froth up, so much as to overflow, unless the vessel be of considerable size; this is very simply avoided by mixing the nitrate of barytes, beforehand, with twice its weight of sulphate of barytes in fine powder. When the nitrate melts, the sulphate gives the mass a degree of consistence which prevents its frothing up, and on boiling the residual mass with water, all the pure barytes dissolves, the sulphate remaining totally unacted on.

If the native carbonate of barytes, $Ba.O..C.O_2$, be strongly heated with carbon, the carbonic acid is converted into carbonic oxide, which passes off, and pure barytes remains behind, $Ba.O..C.O_2$ and C. giving Ba.O. and 2C.O.; the former process is, however, so much easier, that it alone is now usually employed. Graham has suggested the employment of iodate of barytes as a substitute for the nitrate: other processes will be described under the head of sulphuret of barium.

Pure barytes is a heavy gray powder; when exposed to the air, it absorbs water rapidly, giving out much heat, and falling into a fine white powder, *hydrate of barytes*, Ba.O.+H.O. Another hydrate may be obtained crystallized, by dissolving barytes in three parts of boiling water, and allowing the solution to cool slowly; it contains nine equivalents of water. The solution of barytes is very caustic and alkaline; exposed to the air, it absorbs carbonic acid, and a white precipitate of carbonate of barytes is formed; it is hence used to determine the quantity of carbonic acid present in the air (p. 263), and in some other cases.

The detection of barytes is very simple; its soluble compounds give white precipitates with carbonate of soda, with sulphuric acid, and with hydrofluosilicic acid, and none of these are affected by a solution of sulphuretted hydrogen gas in water. The sulphate of barytes is not merely insoluble in water, but also in nitric and muriatic acids, which is a farther characteristic of this earth.

The formula of barytes is Ba.O., and its composition,

Barium,	89·55	One equivalent	=856·9 or	68·7
Oxygen,	10·45	One equivalent	=100·0 or	8·0
	100·00		956·9	7·67

The soluble compounds of barytes are all poisonous, and the carbonate, although insoluble in water, is yet dissolved by the free acids of the stomach, and becomes poisonous. The antidote to all barytic preparations is sulphate of soda, or sulphate of magnesia, administered in excess; the sulphate of barytes then produced is absolutely inert.

Sulphuret of Barium. Ba.S.—This body is of considerable interest, as the source of barytes and of most of its ordinary compounds; to prepare it, sulphate of barytes in fine powder is to be mixed with one fourth of its weight of lampblack, and exposed to a very strong heat for two hours; the carbon removes all the oxygen from the salt; carbonic oxide is evolved, and sulphuret of barium remains; Ba.O. . $S.O_3$ and 4C. giving 4C.O. and Ba.S. The mass thus obtained is to be boiled in water; a deep yellow solution is then produced, from which the sulphuret of barium crystallizes on cooling; it is then a hydrate, but its water of crystallization may be removed by a moderate heat. The sulphuret of barium is decomposed by acids, sulphuret of hydrogen being evolved, and a salt of barytes formed: it is thus that the salts of barytes are obtained for laboratory use.

A simple mode of obtaining caustic barytes directly from the sulphuret of barium has been recently given by Mohr. It consists in adding to a boiling solution of the sulphuret, black oxide of copper, until the whole of the sulphuret of barium is decomposed, as is easily ascertained, by adding a drop of the solution to a solution of acetate of lead; the copper combines with the sulphur, while the barium and the oxygen unite, Ba.S. and Cu.O. producing Ba.O. and Cu.S. This is probably the simplest and cheapest means of obtaining pure barytes.

Of Strontium.

This metal is the basis of the earth strontia, protoxide of strontium, which exists native combined with sulphuric and carbonic acids. The native carbonate of strontia was first found at Strontian in Scotland, and proved to contain an earth different from barytes by Dr. Hope. The similarity of these two earths is very great, so that the general outline of the history of strontia is the same as that of barytes.

The metal *strontium* is obtained precisely as barium, with which it perfectly agrees in character so far as its properties have been ascertained. Its symbol is Sr., and its equivalent number 547·3 or 43·8. To obtain *strontia*, the same processes may be employed which were described for the preparation of barytes, substituting the native carbonate or sulphate of strontia for the compounds of barytes. The strontia is gray, slacks on exposure to the air, forming a hydrate, Sr.O. . H.O., and by crystallization from its watery solution, another hydrate, Sr.O. + 9H.O. Strontia is less soluble than barytes, its taste is not so caustic, nor is it so poisonous

Strontia is distinguished from barytes by tinging the flame of the blowpipe a rich crimson. The red lights used in fireworks owe their colour to nitrate of strontia, which is used in the preparation. Like barytes, the soluble salts of strontia are precipitated by sulphuric acid, but the sulphate of strontia is not so very insoluble as sulphate of barytes; a solution of strontia is also precipitated by carbonate of soda. The hydrofluosilicic and the hyposulphurous acids, which precipitate barytes, do not precipitate strontia, and thus these earths may be distinguished and separated from each other; the chromic acid acts in a similar manner.

The sulphuret and seleniuret of strontium resemble perfectly those of barium, and are prepared in the same way.

Of Calcium.

The existence of this metal was first recognised by Sir Humphrey Davy, it being obtained from lime by the same method as that described under the head of barium; it is white like silver; it sinks in water, which it decomposes rapidly, evolving hydrogen, and uniting with oxygen, forms lime (protoxide of calcium). The symbol of calcium is Ca., and its equivalent number 256 or 20·5.

Calcium combines with oxygen only in one proportion, forming lime, the most important of the earths. It is found very extensively distributed in the mineral kingdom, principally combined with sulphuric and carbonic acids, forming sulphate of lime (gypsum, plaster of Paris) and carbonate of lime (marble, limestone, chalk). These substances exist as rocks or crystallized, the last constituting the mineral species, arragonite and calc spar, often referred to under the heads of crystalline systems, isomorphism, and dimorphism. Lime is found also combined with phosphoric and arsenic acids in several minerals, and the native fluoride of calcium is the fluor spar, used for the preparation of the hydrofluoric acid and other compounds of fluorine.

Notwithstanding the immense quantities of carbonate of lime which are found constituting a great portion of the surface of the globe, as, for instance, the whole centre of Ireland is one vast plain of limestone, and in that as well as other forms, chalk, marble, &c., it is equally extensive in most other countries, it is questionable whether lime should not be looked upon as rather a characteristic of the animal than of the mineral kingdom of nature. The bony or testaceous skeleton, by which the softer portions of the animal frame are attached, is always found to consist of lime united either with carbonic or phosphoric acids, and the diversity of chemical composition in this respect is found to coincide in a remarkable degree with the most natural physiological classification. The skeletons of the vertebrated animals consist principally of phosphate of lime, while in the shells of the invertebrate animals, the carbonate of lime is the prevalent component. The teeth also consist of phosphate of lime; in all these cases, the phosphate of lime is associated with fluoride of calcium, just as occurs in the native phosphate, the mineral apatite.

Now it is remarkable that all the great geological formations which contain carbonate of lime are found to consist of the aggre-

gated skeletons (shells) of myriads of the tribes of invertebrated animals, which had existed in some former period of the world's history. From the densest and hardest limestone to the softest chalk, the entire mass resolves itself ultimately into a congeries of animal remains, and hence the great supply of lime in the mineral state arises from the destruction of its animal sources. Even those crystalline marbles in which no organic remains can be traced, appear destitute of them only from having been subjected, by volcanic heat or otherwise, to the influence of causes which have gradually rendered the texture of the mass completely uniform. The lime which exists in nature must therefore be looked upon as being continually in a state of passage between the organized and the inorganic kingdoms. The plants which grow upon the soil take up, by dissolution in their juices, salts of lime, which pass into the substance of the animal which feeds upon them, and, accumulating in its system, afford materials for the proper development of the skeleton. When the animal dies, the materials of its tissues either serve for the nutrition of some other animal, or, being totally decomposed, its elements return to the mineral kingdom, to be, in after ages, the subject of similar alternations.

Lime is always obtained, for the purposes of chemistry and of the arts, by the decomposition of the native carbonate. To obtain lime perfectly pure, crystals of calc spar or pieces of Carrara marble should be strongly heated in a crucible loosely covered, so that the carbonic acid can readily escape. In the presence of carbonic acid. carbonate of lime is not decomposed by heat, as was explained already in p. 170. On the large scale, lime is obtained by burning the ordinary limestone in kilns. At the bottom is a grate on which fuel is laid, and the kiln then filled with limestone and fuel (culm or small coal), mixed in suitable proportions; when the fire is lighted on the grate, the combustion extends throughout the mass, and as the perfectly burned lime is extracted at the bottom by the orifice of the grate, new quantities of fuel and limestone are introduced above, so that the combustion is continuous; the carbonic acid evolved is completely removed by the rapid draught through the fire.

Lime is a pure white earth. When exposed to the air, it rapidly absorbs water, and falls into a white powder (slacked lime), which is a hydrate, $Ca.O..H.O.$ If a little water be poured on a piece of well-burned lime, it is absorbed instantly, and the lime appears quite dry, but after a few moments cracks, and falls into the powder of hydrate, evolving so much heat as to char wood and inflame gunpowder when in large quantities. It is thus that vessels laden with lime have been burned at sea, by water penetrating to the hold. Lime is soluble in water, though but sparingly, and still less soluble in boiling than in cold water; one part of lime requiring 778 of water at 60°, and 1270 at 212° for its solution; hence, when lime-water is boiled, it becomes turbid. The solution of lime has an acrid, slightly caustic taste; it reacts alkaline; exposed to the air, it absorbs carbonic acid, becoming covered with a crystalline pellicle of carbonate of lime. On breathing into lime-water through a glass tube, it is immediately rendered turbid by the carbonate of lime produced

by respiration; an excess of the carbonic acid, however, dissolves the precipitate. It is in this way that carbonate of lime is held dissolved in almost all ordinary spring and river waters. If lime be perfectly dry, it has little or no tendency to absorb carbonic acid; it requires to be first slacked, and then the hydrate is decomposed, the water being expelled by the carbonic acid; the absorption is very rapid until the lime becomes one half saturated, a compound of $Ca.O..C.O_2+Ca.O..H.O.$ being probably formed, but after that point it advances very slowly.

Lime being a protoxide, its formula is Ca.O., and its composition and equivalent numbers are as follows:

Calcium,	71·91	One equivalent	=256·0	or 20·5
Oxygen,	28·09	One equivalent	=100·0	or 8·0
	100·00		356·0	28·5

Lime is easily distinguished by its dilute solutions not being precipitated by sulphuric acid or sulphate of soda, but giving a white precipitate of oxalate of lime on the addition of a solution of oxalic acid; an excess of oxalic acid does not redissolve this precipitate. The nitrate of lime is deliquescent and soluble in alcohol, in which it also differs from the preceding earths. The compounds of lime, when ignited before the blowpipe, tinge the flame of a brick-red colour.

Lime is of great importance in the arts, from its use in making mortar, and in agriculture from its application as a manure. The lime in mortar is not as carbonate, and its coherent property appears to depend only on the gradual drying of the hydrate by which the stones are retained together, as boards are by the drying of the glue between their surfaces. The use of lime as a manure arises from its decomposing the insoluble organic matters of the soil, woody fibres, ulmine, &c., and producing other products more readily taken up by the radicles of the growing plants. It is hence on such soils as possess a large quantity of organic matter, but are still barren from its not being in the suitable condition, that the beneficial effects of lime are peculiarly marked.

There is a *deutoxide of calcium*, $Ca.O_2$, prepared by adding a solution of deutoxide of hydrogen to lime-water; it resembles deutoxide of barium, but is of no importance.

There are three compounds of sulphur and calcium known; the first, or *protosulphuret of calcium*, Ca.S., may be prepared by heating sulphate of lime to redness in a stream of hydrogen gas, or, more simply, by igniting sulphate of lime with one third of its weight of lampblack; all the oxygen of the salt is carried off as water in the one, or as carbonic oxide in the other case, and the sulphur and calcium remain united. It is a white powder, but very sparingly soluble in water. It plays an important part in the manufacture of carbonate of soda, as will be hereafter explained. When flowers of sulphur and slacked lime are boiled together in water, a deep yellow solution is obtained, which is said to be a sulphuret of lime, but which really consists of a mixture of hyposulphite of lime and *bisulphuret of calcium*, 6S. and 3Ca.O. producing $S_2O_2+Ca.O.$ and $2Ca.S_2$. If the solution be concentrated, this last separates in yellow prisms with water of crystallization. It is from this yellow liquor that the precipitated sulphur is prepared; for, on adding to it an acid, sulphuret of hydrogen is evolved from the sulphuret of calcium in such proportion as to decompose the hydrosulphurous acid, and all the sulphur is precipitated, while the lime remains in combination with the acid which is employed. If the sulphur be in great excess in proportion to the lime, a *pentasulphuret of calcium* may be formed.

The *seleniuret of calcium* is not important. If phosphorus in vapour be passed

through a red-hot tube loosely filled with lime, a brown substance is produced, popularly termed *phosphuret of lime*, but which is a mixture of phosphate of lime and *phosphuret of calcium;* the temperature must not be raised too high, or else the phosphorus may be expelled again. When this phosphuret of calcium is brought into contact with water, it is decomposed, phosphite of lime and phosphuretted hydrogen being produced; this last being evolved in its spontaneously inflammable condition, it is an interesting experiment to throw a fragment of the brown substance into a glass of water; numerous gas bubbles are immediately formed, which explode when they reach the air, as described in p. 300.

Of Magnesium.

This metal, like the bases of the other earths, was first recognised by Humphrey Davy, but the process by which it is best prepared is that given by Bussy. A few pieces of potassium are to be placed at the bottom of a tube of hard glass, and then a quantity of anhydrous chloride of magnesium in small fragments to be laid upon them; the part of the tube containing the earthy chloride is to be heated to near its point of fusion, and the metal converted into vapour by the application of the lamp, as in the figure, p. 321; as soon as the vapour of the potassium comes into contact with the heated salt, vivid ignition ensues, and chloride of potassium being formed, the magnesium is liberated in the metallic state, Mg.Cl. and K. giving K.Cl. and Mg. When the action has ceased and the tube is completely cool, the mass is to be washed with warm water; the chloride of potassium dissolves, and leaves the magnesium, with perfect metallic properties, behind. It is white like silver, malleable and fusible at a red heat; it is not changed by dry air, and but slowly oxidized by damp air; it may be boiled in water without this being decomposed. If magnesium be heated to redness in air or oxygen, it burns with brilliancy, forming magnesia, and it inflames spontaneously in chlorine; it dissolves in dilute acids with the evolution of hydrogen gas, and the formation of a salt of magnesia. The symbol of magnesium is Mg., and its equivalent number is 158·3 or 12·7 according to the standard.

Magnesia, the only known compound of magnesium and oxygen, is a protoxide. It exists in considerable quantity in nature, being a constituent of a great variety of minerals; it is found as hydrate, as carbonate, sulphate, and silicate, but its most abundant source is the magnesian limestone, common both in Ireland and in England, which consists of an equivalent of each carbonate, its formula being $Ca.O..C.O_2+Mg.O..C.O_2$. The pure magnesia is always prepared by exposing the carbonate of magnesia of commerce, the preparation of which will be described among the salts, to a full red heat; the carbonic acid is expelled, and the earth remains pure. Magnesia is a very light white powder, without taste or smell; it is almost perfectly infusible; but it and lime are remarkable for becoming beautifully phosphorescent when strongly heated, and it is hence that lime is used as a source of the most brilliant light when it is heated in the jet of the oxyhydrogen blowpipe. It is very sparingly soluble in water, and still less so in hot than in cold water; its solution browns turmeric paper very slightly. It is remarkably inferior to lime in basic power, but still neutralizes the strongest acids perfectly, forming excellently characterized classes of salts.

The formula of magnesia is Mg.O., and its composition and equivalent numbers are,

Magnesium,	61·29	One equivalent	= 158·3 or	12·7
Oxygen,	38·81	One equivalent	= 100·0 or	8·0
	100·00		258·3	20·7

Magnesia is recognised by its sulphate being very soluble in water, and a solution containing it being precipitated by the alkalies and their carbonates. The precipitate so obtained is redissolved on adding to the liquor a strong solution of sal ammoniac. The most delicate test for magnesia consists in rendering the liquor suspected to contain it alkaline by ammonia, and then adding a solution of phosphate of soda; after a short time the phosphate of ammonia and magnesia crystallizes on the side of the glass, particularly if it be scratched by a glass rod: this double salt is almost completely insoluble in an alkaline liquor. A solid substance containing magnesia possesses the property, that, if it be moistened by a very small quantity of nitrate of cobalt, and ignited strongly by the blowpipe, it becomes a fine pink or rose colour: the presence of other bodies may, however, interfere with this result.

The sulphurets and seleniurets of magnesium are of no importance; they resemble, almost perfectly, those of calcium already noticed.

SECTION II.

METALS OF THE SECOND CLASS.

Of Aluminum.

This metal is prepared by the action of potassium upon its chloride, exactly as described for magnesium in the last division, but the operation must be performed in vessels of platinum or porcelain, as the heat spontaneously evolved during the reaction is so intense as to fuse the most refractory glass; the quantity operated on should likewise be small. A gray melted mass of chloride of potassium and metallic aluminum remains, which is to be washed with cold water, and the metal is thus obtained in minute but brilliant scales.

Aluminum does not decompose water at ordinary temperatures, and only slowly even at a boiling heat, but it dissolves rapidly in dilute acids, and also in solutions of the caustic alkalies, with the evolution of hydrogen gas, from the water being decomposed. The symbol of aluminum is Al., and its equivalent numbers are 171·2 or 13·7, according to the scale.

There is but one compound known of aluminum and oxygen: it is alumina. This earth exists in very large quantity in nature, being even still more abundant than lime; it is a principal ingredient of almost all rocks, except the purest kinds of limestone; it constitutes the great mass of the ordinary clays and soils, these deposites being produced by the gradual decomposition and detrition of various kinds of rocks. In all these forms the alumina is generally combined with silica, and sometimes with sulphuric or phosphoric acids; it is also met with pure, or at least contaminated by the presence of only a trace of foreign matter; thus the ruby and the sapphire, two of the most highly prized precious stones, are alumina, combined with small

quantities of colouring matter. The importance of alumina in the arts is very great; it is a necessary ingredient in the formation of all kinds of earthenware, from tiles or bricks to the finest kinds of porcelain, and is extensively used as the basis or mordant for some of the most brilliant and durable colours that can be fixed upon cotton or woollen cloth. The alumina derives its name from the salt which it forms with potash and sulphuric acid, the *alum* of commerce, from which it is always prepared for the purposes of the chemist.

To prepare pure alumina, a solution of alum is to be decomposed by carbonate of potash, and the precipitate separated by the filter. This precipitate is alumina, the sulphuric acid being taken by the potash, and the carbonic acid, which cannot combine with the alumina, being evolved as gas. The alumina thus produced is, however, not quite pure; it always carries down with it a little sulphate of potash, from which it must be separated by being dissolved in dilute muriatic acid, and again precipitated by carbonate of ammonia; being then well washed, until the water passes from the filter completely free from sal ammoniac, it may be looked upon as pure. The alumina so obtained, when dried at common temperatures, constitutes a bulky gummy mass, which is a hydrate, the earth and the water containing equal quantities of oxygen. To expel this water completely, it must be exposed to a white heat; in drying it contracts very much. It was on the measurement of this contraction that Wedgewood founded his pyrometer, now gone out of use, and to allow for it, all vessels of earthenware and china are made much larger than they are intended to be when completely baked.

In consequence of the great power with which alumina absorbs and retains moisture, it adheres strongly to the tongue, producing a very peculiar sensation when applied to it. The more or less retentive quality of soils results from the same property, and is generally proportional to the quantity of pure clay which they contain.

Alumina is white; if dried at moderate temperatures, it dissolves freely in acids and in solutions of the fixed caustic alkalies, but if it be very strongly heated, particularly if fused by the oxyhydrogen blowpipe, it dissolves much more slowly. It is particularly remarkable for its tendency to unite with organic matters. If a cotton cloth be immersed in a solution of acetate of alumina, the earth will deposite itself completely on the fibres of the cotton, and leave the acetic acid free. The most important processes in calico printing repose upon this principle.

Although alumina is the only compound of aluminum and oxygen, it is yet not to be considered as a protoxide. I have already described, pages 213 and 223, the isomorphous and other relations which establish its constitution to be similar to that of peroxide of iron. It is hence a sesquioxide, and its formula is Al_2O_3. Its composition and equivalent numbers are,

Alumina,	53·3	Two equivalents,	=342·4 or	27·4
Oxygen,	46·7	Three equivalents,	=300·0 or	24·0
	100·0		642·4	51·4

Alumina is easily recognised. Its solution is precipitated by the alkaline carbonates, and the precipitate is dissolved by the caustic

fixed alkalies, but not by ammonia. It is also precipitated white by hydrosulphuret of ammonia. If a solid substance containing alumina be moistened with a trace of nitrate of cobalt, and ignited by the blowpipe, it becomes of a beautiful blue colour.

If aluminum be heated in the vapour of sulphur, it takes fire, and forms a gray mass of *sulphuret of aluminum*. This is decomposed by water, producing alumina and sulphuretted hydrogen, showing that its formula was Al_2S_3, which with 3H.O. give Al_2O_3 and 3H.S. This sulphuret, therefore, cannot be formed in solution; and when a solution of alumina is precipitated by hydrosulphuret of ammonia, as already noticed, the precipitate is pure alumina, and the liquor contains sulphuret of hydrogen.

The seleniuret and phosphuret of aluminum are known, but are of no importance.

Of Glucinum.

The earth of which this metal is the basis has been found but in a few rare minerals, and as it exercises no influence on science from the nature of its compounds, and is of no application in medicine or in the arts, a very brief notice of it will suffice. It exists in the emerald, beryl, and euclase. To obtain it from beryl, the mineral is fused with carbonate of potash, the mass treated with dilute muriatic acid, and evaporated to dryness to separate the silica. The portion which dissolves then in water is to be decomposed by ammonia, which precipitates the alumina and glucina together, and the moist precipitate digested in a strong cold solution of carbonate of ammonia, in which the glucina dissolves. On boiling the filtered liquor so obtained, the glucina separates in combination with carbonic acid, from which it is freed by ignition, and so obtained pure.

This earth is tasteless and inodorous; it is insoluble in water, and has no action on vegetable colours. Its salts taste remarkably sweet, whence its name (γλυκυς). It is easily recognised by its relation to pure and carbonated ammonia, described in the details of its preparation. The metal *glucinum* is prepared from its chloride precisely as aluminum and magnesium, which it resembles very closely in all its properties. Its symbol is G., and its equivalent numbers are 331·4 or 26·5.

Glucina is considered to be, like alumina, a sesquioxide, and its formula being G_2O_3, its composition and equivalents may easily be calculated.

Of Yttrium, Thorium, and Zirconium.

These metals are the bases of earths, concerning which, from the rarity of the sources from which they have hitherto been derived, but little is known, and from their being destitute of scientific importance as well as of practical application, short notice of their characters only need be given.

Yttrium.—The earth *yttria, oxide of yttrium,* exists in some rare Swedish minerals, which were its only sources until the very remarkable discovery, by Apjohn, of its presence in the ordinary Bohemian garnet or pyrope. The method of its extraction is too complicated for description here. It is insoluble in the fixed caustic alkalies, and is precipitated by the yellow prussiate of potash, by which it is completely distinguished from the other earths. It is a protoxide. Its formula is hence Y.O.

Thorium.—The earth *thoria, oxide of thorium,* Th.O., has been found but in two very rare minerals. It is the heaviest of all the earths, its sp. gr. being 9 4. It resembles yttria closely in its properties.

Zirconium.—The earth *zirconia, sesquioxide of zirconium,* Zr_2O_3, is found in two rare minerals, the hyacinth and zircon. It resembles alumina very closely in all its properties, and in some respects assimilates itself to silica, and appears to form the link by which the metallic and non-metallic bodies are connected in this direction. Thus the double fluoride of zirconium and potassium is a sparingly soluble salt, like the fluoride of silicon and potassium, and it is from this double fluoride that zirconium is obtained, by a process identical with that which is described in page 321, for the preparation of silicon.

Cerium. Lanthanum.

These metals are found in a few rather rare minerals, and have been but very recently distinguished from one another. They are always associated together in

nature. Their history does not possess any particular interest, and need hence be noticed but very briefly.

The metallic cerium is obtained by igniting the protochloride of cerium with potassium, as has been already described for other metals. It is a slightly coherent brown powder, which decomposes water slowly, evolving hydrogen, particularly if the water be hot, and forming oxide of cerium. It combines with oxygen in two proportions, forming a protoxide and a sesquioxide, Ce.O. and Ce_2O_3. But all the results obtained with it now require revision, as the discovery of lanthanum has thrown much doubt on the purity of the substances that have been hitherto analyzed as compounds of cerium, and on its received atomic weight. The protoxide of cerium is of a pale fawn colour. If it be heated in the open air, it absorbs oxygen, and changes into the dark brown peroxide; and if this be reduced by hydrogen gas, at a red heat, it forms a yellow complex oxide, probably Ce_3O_4.

Lanthanum.—It was found by Mosander, that by calcining protoxide of cerium so as to convert it into peroxide, only a portion of it became insoluble in dilute nitric acid, and that which dissolved was found, on accurate examination, to be really an oxide of a new metal, which, not forming an insoluble peroxide, may be thus separated from oxide of cerium. From its having been so long hidden in the oxide of cerium usually made, he named it lanthanum (λανθανω), but its detailed history remains yet undeveloped.

Of Manganese.

This metal exists very extensively diffused through nature, although not in very great quantity. Traces of it are found in the animal and vegetable kingdoms, but its great sources are the numerous combinations which it forms with oxygen, and which are employed for the purposes of the arts and of research. Its name is a modification of magnesia, for the native peroxide was once termed *magnesia nigra;* but when the peculiar metal which it contained was recognised, the present appellation was given to it.

Manganese is one of the metals most difficult to reduce, from its great affinity for oxygen, and the high temperature necessary for its fusion. To obtain it, the oxide must be taken in a state of very fine division, and for that object it is best to use an oxide artificially prepared, as described farther on. This is to be mixed with an equal weight of lampblack, and made into a dough with oil, and this mass fixed into a crucible, previously coated with a mixture of clay and charcoal powder. The crucible, so filled, being covered, is to be exposed to the most violent heat of a smith's forge for a couple of hours. On then examining it, a button of metallic manganese will be found occupying its lowest portion.

The metallic manganese is grayish white, granular, and brittle; its sp. gr. 8·013. It is exceedingly infusible. It very soon tarnishes in the air, absorbing oxygen, and falling into a black powder after some time. It decomposes pure water, but very slowly; but rapidly dissolves in dilute sulphuric acid, with the evolution of hydrogen gas, sulphate of the protoxide of manganese being formed.

The symbol of manganese is Mn., and its atomic weight is 346 or 27·7, according to the standard.

It is remarkable for the number of compounds which it forms with oxygen, which are as follows:

Protoxide of manganese	Mn.O.
Sesquioxide of manganese . . .	Mn_2O_3.
Peroxide of manganese	$Mn.O_2$.
Manganic acid	$Mn.O_3$.
Permanganic acid	Mn_2O_7.

In addition, there are two complex oxides:

The red oxide . . . . Mn_3O_4, or $Mn.O.+Mn_2O_3$.
Varvicite . . . . . . Mn_4O_7, or $Mn_2O_3+2Mn.O_2$.

The metallic manganese being of such difficult preparation, the various compounds of it are usually obtained from its most abundant source, the native peroxide, which is sent into commerce in large quantities, to be employed in the arts for the fabrication of chlorine, and in chemistry to prepare oxygen, and many other purposes. The simplest way of preparing the salts of manganese from this native peroxide, which is usually associated with a large quantity of oxide of iron, consists in dissolving it in an excess of muriatic acid, and evaporating the liquor so obtained to dryness. The resulting mass consists of chloride of manganese mixed with perchloride of iron. When this mass is heated to redness, the perchloride of iron is partly decomposed and partly volatilized, and on digesting the residual mass in water, oxide of iron remains undissolved, and a colourless or faintly amethystine solution of protochloride of manganese is obtained. From this the various other preparations may be easily formed.

Protoxide of Manganese—Mn.O.; equivalent 446 or 35·7—may be prepared in many ways. If to a solution of protochloride of manganese an excess of a caustic alkali be added, a bulky white precipitate is produced, which is hydrated protoxide of manganese. In this state it rapidly absorbs oxygen from the air, becoming reddish brown, being converted into red oxide, which is the most permanent of the oxygen compounds of manganese. If any of the higher oxides of manganese, in a state of fine division, such as the red oxide or peroxide artificially prepared, be heated to redness in a tube of hard glass, in a stream of hydrogen gas, oxygen is removed in such proportion as to leave protoxide of manganese behind. The oxide so obtained is of a greenish gray colour; it does not absorb oxygen at all so rapidly as the hydrated oxide; but if it be exposed to the air while hot, it rapidly becomes brown, or even burns. But it is best obtained by mixing together chloride of manganese, carbonate of soda, and sal ammoniac, and exposing them in a kind of platinum crucible to a full red heat. The chloride of manganese is decomposed by the carbonate of soda, chloride of sodium and carbonate of manganese being formed; Mn.Cl. and $Na.O..C.O_2$ giving Na. Cl. and $Mn.O..C.O_2$. The carbonic acid is, however, driven off by the high temperature, and the protoxide of manganese set free, being evolved in presence of the sal ammoniac, which readily yields hydrogen, is prevented from passing to a higher degree of oxidation. The oxide obtained at this high temperature has no tendency to combine farther with oxygen under ordinary circumstances, and may hence be easily preserved.

The oxide is of various shades of grayish green, according to the method of preparation. It is without action on vegetable colours, but it combines with all the acids, evolving in some cases, as with oil of vitriol, intense heat, and forms salts remarkable for their definiteness and neutrality. These salts are generally colourless, but often of a peculiar rose colour, which is not due to the presence of

any higher degree of oxidation, but to a peculiar (isomeric) condition of the salt itself.

Sesquioxide of Manganese.—Mn_2O_3. Equivalent 992 or 79·4. This oxide is found in nature in considerable quantity, either pure, as in the mineral *braunite*, or combined with water, as in the mineral *manganite*. It may be prepared artificially by exposing the peroxide for a short time to a dull red heat, but it is difficult to manage the decomposition of that substance so that it shall not proceed too far. The sesquioxide is of a dark brown colour; exposed to a strong heat it is partly decomposed, evolving oxygen, and being reduced to the state of red oxide. It combines with acids, forming salts which are of a deep red colour, and which are isomorphous with those of alumina. Its salts are immediately decolorized by sulphurous acid and by sulphuretted hydrogen. This oxide possesses the property of staining glass purple or violet, and by this character an exceedingly small trace of manganese can be detected by fusing the substance with borax in the oxidating flame of the blowpipe.

Peroxide of Manganese, or Black Oxide.—$Mn.O_2$. Equivalent 546 or 43.7. This substance, which is the most abundant source of manganese, and that from which all its technical applications are derived, exists in nature in a variety of forms. Crystallized and pure, it forms the mineral *pyrolusite ;* combined with water, $2Mn.O_2+H.O.$, it constitutes the mineral *Wadd*, which,in an impure form, contaminated with variable quantities of peroxide of iron, carbonate of lime, and carbonate of barytes, forms the earthy varieties, which are those usually found in commerce. This oxide may be prepared artificially by decomposing the protochloride of manganese by a solution of chloride of lime, $Mn.Cl.$ and $2Ca.O.+Cl.$ producing $2Ca.Cl.$ and $Mn.O_2$. It is also produced when permanganate of potash is decomposed by any organic substance. In these cases it is precipitated in combination with one equivalent of water, $Mn.O_2+H.O.$, from which it may be freed by a temperature below redness.

This peroxide of manganese is black ; exposed to heat, it abandons oxygen, being reduced first to the state of sesquioxide, and finally to that of red oxide. It does not unite with either acids or alkalies ; but, when heated with strong sulphuric acid, it is decomposed in the manner fully described under the head of oxygen, in page 244. Its use in the preparation of chlorine has been also noticed, page 301. An important object to which it is applied is to peroxidize the iron contained in the ordinary materials used in the manufacture of glass. If the iron were as protoxide, it would colour the glass green ; but the red oxide produces only a very faint yellowish tinge ; and as the protoxide of manganese is itself destitute of colouring power, by the action of $Mn.O_2$ on $2Fe.O.$ there are formed $Mn.O.$ and Fe_2O_3, two substances which have no injurious effect upon the glass ; if, however, the peroxide of manganese be added in excess, a purple colour is produced.

Of the complex oxides, the red oxide is alone of interest. It is the most stable of the compounds of manganese ; and whenever the quantity of this metal present in a substance is to be determined by analysis, it is always as the red oxide that it is obtained. A solution of any salt of manganese, being precipitated by an excess of a caus-

tic alkali, the precipitate, cautiously washed and ignited in an open crucible, gives the quantity of red oxide corresponding to the quantity of manganese present. The varvacite, the other complex oxide, is a mineral of rare occurrence, and only of interest as it may be mistaken for the peroxide, to which it is inferior in technical value.

The peroxide of manganese found in commerce is never quite pure; and as its use in the arts, and, consequently, its price, are, generally speaking, due exclusively to the quantity of oxygen it is capable of yielding, a ready mode of effecting its analysis becomes of great importance. There are two modes in which this may be accomplished upon very simple principles, and in a short time, with sufficient accuracy for all practical purposes. The first consists in converting oxalic acid into carbonic acid, by means of the second atom of oxygen which the peroxide of manganese contains; for $Mn.O_2$ and C_2O_3 produce $Mn.O.$ and $2C.O_2$. For this purpose 100 grains of the manganese are to be introduced into a weighed flask, and 150 grains of oxalic acid, dissolved in 500 grains of water, are to be then poured upon it; to this 350 grains of oil of vitriol are to be added, and the orifice of the flask closed by a cork, through which passes a tube containing fragments of recently-fused chloride of calcium. The weight of this cork and tube are to be included in the tare of the flask. On the addition of the oil of vitriol, a brisk effervescence takes place, owing to the escape of carbonic acid gas, which, passing over the fragments of chloride of calcium in the tube, are dried, so that the gas alone passes off. When the action slackens, a gentle heat may be applied until all the oxide of manganese has dissolved; a small quantity of a light brownish sediment, which generally forms, is easily distinguished from the particles of black oxide: as soon as the action is quite over, the flask is suffered to cool, and as it contains still a quantity of carbonic acid gas, this is removed by taking out the cork, and blowing air into the flask gently by a glass tube; the cork is then to be replaced, and the flask, with its contents, weighed. It is found to be lighter than it and the materials together had been, and the loss is the carbonic acid. The quantity of carbonic acid formed is thus found, and the quantity of oxygen it contained calculated; one fourth of this had been derived from the peroxide of manganese by its conversion into protoxide, which remains combined with sulphuric acid in the liquor, and the quantity of peroxide in the 100 grains of the ore is thus directly found. Thus, taking as an example an actual determination, the flask and materials weighed altogether 1876 grains; after the action had terminated it weighed 1816·5 grains; the loss was, therefore, 59 5. This consisted of 16 3 of carbon and 43·2 of oxygen. The oxygen derived from the mineral was, therefore, $\frac{43 \cdot 2}{4}=10 \cdot 8$, which represent 59 grains of pure peroxide of manganese in the 100 of the substance used.

The second mode of analysis consists in treating a certain quantity of the native oxide with an excess of muriatic acid, and passing the chlorine so evolved through water in which lime is diffused; chloride of lime is formed. A certain quantity of protosulphate of iron (green copperas) is to be dissolved in water, and the solution of chloride of lime added thereto, until the iron liquor ceases to strike a blue colour with a drop of solution of red prussiate of potash; then comparing the quantity of the solution of chloride of lime required with the quantity that was produced, the total quantity of chlorine generated, and, hence, the total quantity of oxygen available in the mineral, are known. The theory of the process may be still more simply expressed by the formulæ of the bodies engaged, as follows: $Mn.O_2$ and $2H.Cl.$, acting together, produce $Mn.Cl.$ and $2H.O.$, while $Cl.$ is given off as gas; this combines with $Ca.O.$ When the compound $Ca.O.Cl.$ is brought in contact with $2(Fe.O..S.O_3)$, the oxygen passing from the lime to the iron, we have $Ca.Cl.$ and $Fe_2O_3.2S.O_3$ produced. As long as any protosulphate of iron exists, the solution gives Prussian blue with the red prussiate of potash; but when all the iron is changed to peroxide, the blue colour is no longer produced. The following example of an actual operation will complete this explanation. 100 grains of commercial oxide of manganese were placed in a flask with about one ounce of strong spirits of salt, and the chlorine evolved was conducted by a bent tube to the bottom of a deep jar containing 1600 grains of water with 100 grains of slacked lime; when the oxide of manganese had been completely decomposed by the muriatic acid, and all evolution of chlorine had ceased, a quantity of the solution of chloride of lime was filtered for use; this being very strong, 500 grains of it were diluted with 1000 of water. On the other hand, 100 of crystallized protosulphate of iron were dissolved in 1000 grains of water, and the dilute solution of chloride of lime added thereto by drops

from an accurately graduated tube, until, by the test of red prussiate of potash, all the iron was peroxidized. It required 1300 grains of the dilute solution, and hence 433 of the strong solution. Now, as 100 grains of the mineral had given 1600 grains of this strong solution, the 433 grains corresponded to 27 grains; the available oxygen of which was exactly equivalent to transfer the iron of the protosulphate to the state of peroxide. Now the 100 grains contain 45·6 of water, 28·9 of acid, and 25·5 of protoxide of iron, consisting of 19·7 of iron and 5·8 of oxygen, and it requires one half more, that is, 2·9, to form peroxide. The result is, that in the 27 grains of commercial oxide of manganese, the available oxygen is 2·9, and the quantity of pure peroxide consequently 15·8 grains, or 58·7 per cent. This whole process, although, when thus described in detail, it may appear complex, is exceedingly simple in execution, and does not occupy much time. In accuracy, the two methods are about equal, giving results which may be depended on to one per cent.

A mode has been recommended, which consists in simply adding the green sulphate of iron directly to the muriatic acid and oxide of manganese in the flask, until the salt is found to be slightly in excess by the filtered liquor giving Prussian blue with red prussiate of potash; the quantity of green copperas added is known by having previously weighed out a quantity, and then weighing what may remain after the process has been completed. If no chlorine could escape the action of the iron salt, this method would be much the shortest and simplest that could be employed; but it is exceedingly difficult so to manage the decomposition as to avoid its partial loss. On this account, I look upon this method as inferior in accuracy, and really not much simpler of execution, than those previously described.

The composition of the commercial oxide is very variable, but the general limits may be considered as being between 60 and 70 per cent. of pure peroxide in 100. Frequently, the commercial substance contains sesquioxide, or one of the complex oxides; but in all these cases, the methods given, as they determine the quantity of available oxygen, show the true value of the specimen, no matter what the state of combination of the metal may be.

Manganic Acid.—$Mn.O_3$. Equivalent 646 or 51·7. If peroxide of manganese be mixed with caustic potash, or carbonate or nitrate of potash, in a crucible, and ignited strongly, a green fused mass is obtained, which dissolves in a small quantity of water with a fine grass-green colour. After some time, particularly if the solution be diluted, it gradually changes colour, a brown precipitate separates, and the liquor becomes of a splendid red colour. This substance first got the name of *mineral chameleon* from these changes, but their production is now known to depend on the formation of two distinct acids of manganese. The peroxide of manganese in these cases combines with another atom of oxygen to form manganic acid, which unites with the potash. If potash, caustic or carbonated, be used, the oxygen is derived from the air; if nitre, it supplies oxygen; but the best source consists in mixing four parts of peroxide of manganese in fine powder with 3½ parts of chlorate of potash, and adding thereto five parts of caustic potash dissolved in a small quantity of water. This mixture is to be evaporated to dryness, powdered, and afterward ignited in a platinum crucible, at a low red heat insufficient for fusion. By digestion of this mass in cold water, a deep green solution is obtained, from which, by evaporation in vacuo, the manganate of potash is obtained in crystals. The salts of this acid are isomorphous with those of the sulphuric and chromic acids. They are decomposed very easily, particularly if organic matter be present, and the acid itself is hence incapable of being exhibited in an isolated form.

Permanganic Acid.—Mn_2O_7. Equivalent 1392 or 111·4. When a solution of manganate of potash is diluted with boiling water, a copious precipitate of hydrated peroxide of manganese forms, and a

fine crimson solution of permanganate of potash is obtained. $3Mn.O_3$ produces $Mn.O_2$ and Mn_2O_7. By rapidly evaporating this solution until a pellicle forms, an abundant crop of crystals of permanganate of potash is obtained on cooling: these are isomorphous with the perchlorate of potash, and are almost completely black, but with a very peculiar bronze lustre. The salts of this acid are very stable, and by treating the permanganate of barytes with a proper quantity of dilute sulphuric acid, a deep crimson solution of permanganic acid is obtained. This acid cannot be had solid, according to Mitscherlich, its solution when heated to 100° F. being decomposed into peroxide of manganese and oxygen gas. It is very probable that the solid substance described as dry permanganic acid by some chemists contained some other matter combined with it.

The formation of these acids by the action of sulphuric acid on peroxide of manganese has been already noticed, and the most delicate test of the presence of manganese in minerals consists in fusing a fragment of the substance with a little carbonate of soda on a slip of platina foil, by means of the oxidizing flame of the blowpipe. The mass, on cooling, becomes apple-green, from the formation of manganate of soda, if there be the smallest trace of manganese in the substance used.

There is but one sulphuret of manganese. It is found as a mineral, and formed also by heating oxide of manganese and sulphur (page 285). It is precipitated in a hydrated state, when a solution of manganese is decomposed by hydrosulphuret of ammonia. Its colour is then flesh red. Its formula is $Mn.S$.

The detection of manganese is very simple. When in a solid form, its compounds are recognised by giving before the blowpipe a purple glass with borax, and a green bead with carbonate of soda. In solution, if the manganese be as protoxide, the solution is colourless, and yields with the caustic alkalies a white precipitate ($Mn.O.$), rapidly becoming brown (Mn_3O_4): with the alkaline carbonates, a white precipitate, $Mn.O. . C.O_2$; and with hydrosulphuret of ammonia, a flesh red hydrated sulphuret. The yellow prussiate of potash precipitates the salts of manganese pure white, if there be no trace of iron present. When the manganese is not in the state of protoxide, the solution is always coloured red or green. These solutions are decolorized by sulphurous acid and by sulphuretted hydrogen, which absorbs oxygen from all the higher degrees of oxidation, and a colourless solution of protoxide is then obtained, which gives the reactions already described.

SECTION III.

METALS OF THE THIRD CLASS.

Of Iron.

This is the most extensively distributed, and also the most important of the metals; it may, indeed, be considered as being, after those elements necessary to the functions of animal existence, that which is most indispensable to man for the wants of ordinary life. On its employment and applications is founded every important

step which marks the gradual progress of the human race from bar barism to civilization. The difficulties which its reduction from the state of ore present, the variety of conditions necessary for its being successfully wrought into useful forms, and the pre-eminent advantage it possesses over every other metal for the construction equally of the simplest tool and the most complex machine, for the implements of war as well as peace, all combine to excite the energies of a people to its acquisition, whether by their own labour or by commerce; and thus impel them to mental activity and civilization, either of native and independent growth, or borrowed from more advanced neighbours. As gold and jewels hence become the type of ignorant and barbaric pomp, so iron may be regarded as the greatest material source of national intelligence and industry.

Iron exists in nature under a variety of forms; it is found native; for, in addition to loose blocks of metallic iron found on the surface in various countries, and to which a different nature may be assigned, it is found in veins, in mines, in Russia and America. Its most abundant form is that of oxide, either pure, forming the various black and magnetic oxides, the hæmatite, or red oxide, &c., or combined with carbonic acid, constituting the clay iron stone from which the iron of commerce is principally extracted. Its sulphurets are also found in abundance, and native arseniates, phosphates, sulphates, and other salts have been found.

A most remarkable source of iron is one not truly terrestrial, but that, occasionally, masses appear in our atmosphere at great heights above the surface, and presenting all the appearances of vivid ignition and combustion; they move generally with great velocity obliquely towards the ground, and generally, before touching, or at the moment of contact with the surface, burst with an explosion, scattering their fragments to considerable distances. These masses are termed *ærolithes;* they consist, in general, of an alloy of iron, with some nickel and chrome, with traces of other metals, and are generally invested with a vitreous glaze of earthy matter, which is constituted of minerals (olivine and pyroxene) found native in volcanic rocks. The only theory which can explain the origin of these meteors is, that they are expelled violently from the active volcanoes which telescopic research has proved to exist in great numbers on the surface of the moon, and that, passing beyond the limits of the attraction of our satellite, they come under the influence of this earth, and fall towards its surface. No such substances are ever found projected from terrestrial volcanoes.

The general principles of the smelting of the clay iron stone have been already noticed (p. 334), both considering it as a mere carbonate of iron, and where it contains clay, silica, and alumina, so as to render lime necessary as a flux. It is, however, a remarkable property of iron—one on which rests, perhaps, its most useful applications—that the metal so obtained is not pure. The iron, when reduced, combines with a quantity of carbon, generally about five per cent., approximating to the formula $C.+4Fe.$, and forming cast iron, which is easily fusible, while the pure metal is almost quite infusible. The cast iron is, however, not by any means a pure carburet of iron; it contains small quantities of silicon and phosphorus,

according to the proportions of which it varies in properties, so as to constitute a number of varieties, known in the arts by their colour and texture, but of which it would be superfluous to speak here. When cast iron remains under water for a considerable time, it becomes gradually oxidized, magnetic oxide of iron being formed, and the carbon remaining under the form of a spongy mass, preserving, even in minute details, the figure of the original mass.

Cast iron has a great tendency to crystallize in becoming solid, and then expands powerfully; hence its property of filling up the most minute crevices of moulds into which it is poured in the liquid state, and its multifarious uses for making castings, from whence it derives its name.

Pure or malleable iron is made from cast iron by taking advantage of the fact that, though iron and carbon are both combustible, yet carbon is the more so of the two. Hence, if cast iron be melted in a reverberatory furnace (see p. 333), and exposed to a current of air, the carbon is gradually burned out, the metal becomes less and less fusible, and ultimately breaks up into an incoherent granular mass like sand; by then increasing the heat, these grains agglutinate, and are worked up into a ball about the size of a large loaf, which is taken out of the furnace on a shovel, and subjected to great pressure by machinery. The soft, pasty particles of malleable iron are thus welded to each other, and any portions of liquid, unaltered cast iron that might remain are squirted out, as water would be by pressure from the pores of a sponge; this lump of malleable iron is then passed through a succession of rollers, driven by powerful steam engines; each pair of rollers having a smaller interval than the preceding, the mass is gradually elongated into a bar, and finally is delivered, at the end farthest from the furnace, in the form of the soft bar iron of commerce. The heat evolved by the enormous pressure to which the metal is subjected in this process is so great, that the bar remains soft enough to be moulded by the rollers all through its passage.

This process by the reverberatory furnace is termed *pudling*, and has been very much improved lately by burning out the carbon by means of a certain quantity of oxide of iron or oxide of manganese. Thus, by heating together two parts of cast iron and one of scales of black oxide of iron from a forge, all the carbon and oxygen pass off as carbonic acid, and the iron of both remains pure. Fe_3O_4 and Fe_8C_2 produce Fe_{11} and C_2O_4.

The bar iron thus obtained differs remarkably from the cast iron in all characters: it is soft, flexible, ductile, and malleable, none of which properties cast iron possesses. It fuses only at the very highest temperatures, and then becomes only semifluid. It is, consequently, quite impossible to run it into moulds. It possesses, however, the important character of *welding* at a white heat; that is to say, it assumes a doughy consistence, so that several pieces of it, laid together, may be kneaded into one by blows of a hammer or by pressure between rollers, so as to form a single mass, the points of junction being totally undistinguishable. It is thus that soft iron is always worked at a white heat. Its strength is much increased by several pieces being thus welded together, and hence

all parts which require to possess peculiar tenacity, such as anchors, &c., are always made, not in a single piece, but by thus welding together a bundle of small bars.

A third and equally important form in which iron exists in the arts, is that of *steel*. Steel is intermediate to cast iron and bar iron in constitution, containing generally about 1·5 per cent. of carbon. Steel may be formed directly from the ore or from cast iron by proportioning the action of the fuel and of the air in the furnaces so as to leave combined with the iron as much carbon as constitutes steel. But the most important and curious mode of making steel is by what is termed *cementation*. Bars of iron are laid in boxes, imbedded in powdered charcoal, and exposed for some hours to a full red heat; the carbon gradually penetrates through the whole substance of the iron, changing it into a bar of steel of pretty uniform structure. The bar becomes frequently blistered from gas bubbles forming in its substance. This process can be effected even though the carbon may not directly touch the iron, provided oxygen be present; carbonic oxide being formed, which is decomposed by the iron, half the carbon being absorbed, and carbonic acid given off. It is the escape of this last gas under the form of bubbles that produces the blistering of steel. The decomposition of the carbonic oxide takes place at the surface of the bar in great part, but the carbon is transferred from particle to particle of the iron until the entire mass assumes the same constitution. Steel is harder and more fusible than pure iron, but its peculiar hardness is given to it only when it has been heated to redness and suddenly cooled; it is then exceedingly brittle, hard, and elastic, and is thus fitted for its extensive use in cutting instruments, pivots, files, &c. The steel, when it has cooled slowly, is so soft that it is easily engraved upon, cut, and may be welded with soft iron; the instrument being so constructed, it is heated to redness and suddenly cooled; it is thus hardened, but is still unfit for being employed until it is *tempered* to the particular use for which it is destined by being heated in oil to a certain degree, and then allowed to cool slowly. By this means the excess of hardness is got rid of, and the steel remains of the quality required.

The peculiar property of iron and steel of becoming magnetic, has been described in page 143. Not only is iron in the pure state, and when combined with carbon, attracted by the magnet, but several of its oxides and sulphurets possess the same character; of these, one constitutes, indeed, the natural magnet, the native *loadstone*.

Pure iron is bluish white, exceedingly brilliant, very malleable and ductile; it is the strongest of all the metals. Its specific gravity is 7·8. It becomes pasty when intensely heated, whence its remarkable power of welding, which belongs, besides, to platinum and sodium.

When iron in mass is exposed to dry air, it does not become oxidized; but when in a state of very minute division, it takes fire when gently warmed, and burns, forming peroxide of iron; when strongly heated in oxygen gas, as by attaching a little sulphur or a bit of taper wick to a wire, and plunging it into a vessel of oxygen,

it burns with exceeding brilliancy, and forms globules of black oxide of iron, Fe_3O_4. The true product of the combustion is peroxide, Fe_2O_3, but this loses one ninth of its oxygen by the intense temperature, and forms the black magnetic oxide. It is hence that, when iron is burned in oxygen gas, the oxide, which is thrown off in minute grains, collects on the inside of the jar as peroxide, but the larger globules, which are intensely heated for some time before they melt off the wire, are reduced to the state of black oxide. It is not quite certain whether iron decomposes water in the absence of an acid, but the presence of a small quantity even of carbonic acid produces decided action, and hence the rapid corrosion of iron in damp air, forming carbonate of iron (rust). In dilute sulphuric acid iron dissolves with great rapidity, evolving hydrogen, which, however, is very impure, for even the softest iron contains traces of carbon, which combines with some of the hydrogen, forming compounds, which give the gas a peculiar odour, and colour its flame yellow At a red heat water is decomposed rapidly by iron, as fully described in p. 246. If iron be immersed in water holding potash, lime, or soda in solution, or if the iron be covered up in quicklime, all rusting is prevented, probably from any carbonic acid present being totally taken up by the base.

A remarkable property of iron, though not absolutely peculiar to it alone, is, that when placed in contact with the hydrated nitric acid, sp. gr. 1·35, it may remain unacted on, becoming *passive;* although, under ordinary circumstances, it is rapidly dissolved by that acid with evolution of nitric oxide. This passive condition may be produced in many ways. 1st. If one end of a long iron wire be ignited, and then, when cool, the wire be immersed in the acid, the ignited end being dipped first, it remains unaltered. 2d. If a piece of platina wire be fastened to a piece of iron wire, and then immersed in the acid, the platina first. 3d. By placing a platina wire in the acid, then immersing an iron wire in contact with it, the platina wire may be withdrawn, and the iron wire remain passive. 4th. By making the iron wire the positive pole of a galvanic battery. 5th. By contact with a wire already passive; thus, an iron wire being immersed in the acid, as in No. 3, another wire may be put in contact with it, and the first then withdrawn, and so on for an unlimited succession of wires. These are not the only methods, but merely the most remarkable.

The properties of iron thus rendered passive are curious. It appears to have lost all tendency to unite with oxygen; it does not dissolve in acids; it does not precipitate copper from its solutions; and when used as a positive electrode for a voltaic battery, oxygen is evolved from it precisely as if the electrode had been platinum. We do not as yet know the true theory of these effects. The most available explanation is, that the iron, by an alteration of molecular structure, assumes a condition by which it becomes similar in its electrical relations to the noble metals. It is possible that this property may be connected with the equivalency of two equivalents of the iron and manganese group of metals to one of chlorine, and that when, by a change of molecular arrangement, like isomerism,

the particle becomes Fe_2 in place of Fe., it is incapable of acting as the positive element in galvanic or chemical combinations.

The equivalent of iron is not so accurately known as those of metals much less important and less common. The best determinations make it about 339 upon the oxygen, and 27·2 upon the hydrogen scale. Its symbol is Fe., from its Latin name.

Oxides of Iron.—Iron combines with oxygen in two proportions, forming a protoxide and a sesquioxide, and these, again, unite to form complex oxides, the black or magnetic oxides of iron.

Protoxide of Iron.—Fe.O. Equivalent 439 or 35·2. This oxide cannot be obtained pure in a dry state, from the rapidity with which it absorbs oxygen. It exists as the basis of a very extensive class of salts, the green or protosalts of iron. From their solutions, it is precipitated by an alkali as a white hydrate, which rapidly becomes green, and finally brown-red, from absorption of oxygen. If we attempt to form the protoxide by processes similar to those described for obtaining protoxide of manganese, the iron is reduced either to black oxide or to the metallic state. This oxide exists native, combined with carbonic acid, in the common carbonate of iron, and is the form in which the metal exists, dissolved in all chalybeate springs.

Peroxide of Iron.—Fe_2O_3. Equivalent 978 or 78·4. This substance exists in very great abundance in nature, crystallized in rhombohedrons, being isomorphous with the crystallized alumina, corundum. This, the *ologist iron*, constitutes the celebrated Elba iron ore. It forms, in a more or less hydrated condition, the *hematite*, of various shades of red and brown, from which a great deal of the best iron and steel is made. It exists in a variety of minerals, and forms the red or yellow colouring matter of clay and of the different kinds of ochres. I have noticed that when iron is burned in a full supply of oxygen, this red oxide is formed, and it is produced also when iron rusts, for the protocarbonate which first forms is gradually decomposed, abandoning its acid, and absorbing oxygen. It is thus that the margins of chalybeate springs become coated with an ochrey deposite; the carbonate of iron originally dissolved being gradually converted into red oxide, while the carbonic acid passes off.

The peroxide of iron may be artificially prepared by precipitating a solution of any of its salts with an alkali caustic or carbonated. In the latter case, the carbonic acid is given off, as the peroxide of iron does not combine with it. The hydrated peroxide which is precipitated is of a light reddish-brown colour, but when dried it becomes dark brown. Strongly ignited, it becomes nearly black; and, indeed, by an intense heat it loses some of its oxygen, $3(Fe_2O_3)$ giving $2(Fe_3O_4)$, and O. escaping, being decomposed just as the sesquioxide of manganese, but requiring much greater heat. The peroxide of iron combines with acids to form salts, which are all acid, and easily decomposed. They will be described hereafter. Its chemical combinations resemble those of alumina and sesquioxide of manganese, with which they are isomorphous.

When a solution of a protosalt of iron is exposed to the air, it gradually absorbs oxygen until two thirds of the iron become peroxidized, and then the decomposition ceases. The liquor then contains a compound oxide, $Fe.O. + Fe_2O_3$, and on the addition of a caus-

tic alkali this is precipitated as a black powder, which, when dry, is powerfully attracted by the magnet. This is the artificial magnetic oxide of iron. It may be prepared at will by taking three equal portions of protosulphate of iron, and peroxidizing two of them by means of a little boiling nitric acid, then mixing the solutions, and precipitating the whole by water of caustic ammonia. The precipitate is a hydrate, but may be deprived of the water without alteration.

This magnetic oxide of iron exists native in great abundance; it constitutes the common loadstone, and is that produced when iron is oxidized at high temperatures. It thus constitutes the scales of iron which form in smithies and forges during the successive heatings and hammerings to which the metal is subjected. These scales of iron are, however, not uniform in constitution, and are hence inferior as a steady medicinal agent to the oxide artificially prepared by precipitation.

Sulphurets of Iron.—Sulphur combines with iron in three proportions, forming the protosulphuret, the sesquisulphuret, and the bisulphuret. These again combine, so as to produce complex (magnetic) sulphurets. Other degrees (subsulphurets) are problematical.

Protosulphuret of Iron.—Fe.S. Equivalent 540·4 or 43·3. The affinity of iron for sulphur is very remarkable. If a rod of iron be heated to whiteness, and then touched to a stick of sulphur, they combine with energy, and the sulphuret of iron flows down in copious drops. If vapour of sulphur be made to gush from a jet, and an iron wire heated to bright redness be placed in it, it takes fire, and burns with scintillations as brilliantly as if it had been immersed in oxygen gas. In these cases, where the iron is in excess, the protosulphuret is formed. It is most conveniently prepared by heating together to bright redness, in a crucible, three parts of iron filings or turnings, and two of sulphur; at a high temperature the resulting mass may be fused. This compound is black, its fracture yellowish. It dissolves in dilute acids, evolving sulphuret of hydrogen, and forming a salt of protoxide of iron. This is almost its only use in the laboratory. The manner of obtaining sulphuret of hydrogen from it has been described in page 292. This protosulphuret of iron exists sometimes, though rarely, in nature, and is dangerous, particularly in coal mines, from the avidity with which, when moist, it absorbs oxygen, forming protosulphate of iron, Fe.S. and 4O. giving Fe.O. . $S.O_3$; during which process it occasionally becomes so heated as to set fire to the beds of coal near it, and thus cause considerable loss.

This sulphuret may be prepared in the moist way by adding hydrosulphuret of ammonia to a protosalt of iron. Thus Fe.Cl. and $S.H.+N.H_3$ produce Fe.S. and $Cl.H.+N.H_3$. It is a jet black powder, which dissolves readily in acids, and when exposed moist to the air, rapidly absorbs oxygen, forming green copperas.

Sesquisulphuret of Iron.—Fe_2S_3. Equivalent 1282 or 102·7. This compound, which corresponds to the peroxide, is very instable in constitution. It may be prepared in the moist way by adding to a persalt of iron in solution, hydrosulphuret of ammonia. A black precipitate forms, which may be dried in vacuo. It may be also

produced by heating peroxide of iron in a current of sulphuretted hydrogen gas, water being formed. It is not attracted by the magnet. It dissolves in acids, but one third of the sulphur is precipitated, two thirds only combining with hydrogen, and the iron existing in solution as a protosalt. Thus Fe_2S_3 and 2H.Cl. give 2(Fe.Cl.) and 2H.S. with deposition of S. This arises from the circumstance that peroxide of iron is reduced by sulphuretted hydrogen to protoxide, water being formed, and sulphur set free.

Bisulphuret of Iron.—$Fe.S_2$. Equivalent 741·5 or 59·4. This substance is met with in very large quantity in nature, constituting the iron pyrites used in the manufacture of sulphuric acid and of copperas. It is dimorphous (pages 229–232), and in its two forms possesses very different properties. It may be prepared artificially by heating together the protosulphuret in a state of minute division, with half its weight of sulphur. When the excess of sulphur has been distilled off, there remains a voluminous yellow powder, not acted on by the magnet, and insoluble in acids, which is the bisulphuret of iron. This bisulphuret of iron is found in a variety of forms, which belong properly to the different kinds of native oxides of iron, which being probably acted on by vapour of sulphur from volcanic sources, have lost their oxygen, and, without being melted, have changed into bisulphuret. It is also found simulating the figures of a variety of organic remains, as nautili, &c., where, probably, the animal having perished in water holding traces of sulphate of iron in solution, the hydrogen compounds evolved by its decomposition have reacted on the sulphate of iron, abstracting its oxygen and producing a deposite of pyrites.

Magnetic Sulphurets of Iron.—Of these the most remarkable is that which corresponds to the magnetic oxide, having the formula Fe_3O_4=Fe.S.+Fe_2S_3. It is found native at Barege, and may be formed by exposing to a red heat, in close vessels, the bisulphuret or sesquisulphuret: the pyrites $3(Fe.S_2)$ producing Fe_3S_4 and S_2, precisely as peroxide of manganese $3(Mn\,O_2)$ produces O_2 and Mn_3O_4. If, however, the heat be raised too high, more sulphur is expelled, and another kind of magnetic sulphuret, Fe_7S_8=5Fe.S.+Fe_2S_3, formed, which is also found native, and which corresponds to the black scales of oxide of iron, which are 5Fe.O.+Fe_2O_3. This compound is always formed in making the protosulphuret, if there be an excess of sulphur above the proper proportion used.

The seleniuret and phosphurets of iron resemble very closely the sulphurets. Phosphuret of iron exists generally in cast iron in small quantity.

The detection of iron is very simple. It may exist in solution in the state either of protoxide, black oxide, or peroxide; and as the application of reagents becomes much simpler in the last case, it is best, when the object is only to ascertain the presence or absence of iron, to boil the solution with a few drops of nitric acid, by which any iron that may be present is peroxidized.

A solution containing peroxide of iron produces with water of ammonia a reddish-brown precipitate of hydrated peroxide; with yellow prussiate of potash, a fine Prussian blue; with sulphocyanide of potassium, a deep blood-red colour, but no precipitate; with

a solution of tannin or tincture of galls, a deep violet or black. With sulphuret of hydrogen there is no effect except the separation of a deposite of pure sulphur, but with hydrosulphuret of ammonia a black precipitate of sesquisulphuret of iron.

If the solution contain the iron only as protoxide, ammonia produces a precipitate, at first whitish, but rapidly becoming bluish-green. The yellow prussiate of potash, a precipitate, at first white, but rapidly becoming blue. The sulphocyanide of potassium, the tannin, and the sulphuret of hydrogen are without effect, but the hydrosulphuret of ammonia forms the black protosulphuret. The characteristic reagent for protoxide of iron is the red prussiate of potash, which gives Prussian blue, but does not act upon the solution of peroxide.

If the solution contain at the same time both oxides, the precipitate by ammonia is, from the commencement, green or black, and all the other reagents concur in the demonstration of the presence of the two states of oxidation of the metal.

Of Nickel.

An ore which, from its external characters, was supposed by the German miners to contain copper, but resisted all endeavours to extract that metal from it, received the name of *kupfer-nickel*, or deceitful copper. Subsequently it was found to consist of a peculiar metal united to arsenic, and this metal retained the name *nickel*, its meaning being forgotten or lost sight of. A substance found in commerce, termed *speiss*, a residue from the manufacture of smalts, is also an arseniuret of nickel, and from either of these sources the metal is generally extracted.

The mass containing nickel and arsenic is dissolved by a mixture of nitric acid and sulphuric acid, diluted with water. By this means the nickel is converted into sulphate of its oxide, and the arsenic into arsenious acid. On concentrating the liquor, most of the latter is got rid of by crystallization. Carbonate of potash is then to be added to the liquor, until the green precipitate which first forms ceases to be redissolved. On then evaporating and cooling, a double sulphate of nickel and potash is obtained, which, by two or three recrystallizations, is freed from all traces of arsenic. This double salt may, however, be contaminated by iron and copper; from the first it is separated by sulphuretted hydrogen, and from the last by the solubility of the oxide of nickel in water of ammonia. From the ammoniacal solution, the oxide of nickel may be precipitated by oxalic acid, as an insoluble oxalate, which, when dried and heated, gives off carbonic acid, and leaves metallic nickel, $Ni.O.+C_2O_3$, producing $2C.O_2$ and Ni. The metallic nickel is then in the form of a very light sponge.

It is somewhat more fusible than cast iron; of a silvery white colour. It does not rust when exposed even to damp air. Its sp. gr. is about 8·5. It is nearly as magnetic as iron, and retains its magnetism, resembling in that respect steel rather than pure iron. In its permanency of lustre, nickel resembles the precious metals, and its alloys are of singular brilliancy and whiteness. It is hence that, added to brass in the proportion of one to five, it is employed as a substitute for silver, constituting the German silver, nickel silver, argentine, and British plate of commerce, as well as the packfong long used in China.

The symbol of nickel is Ni.; its equivalent 369·7 or 29·6.

Oxides of Nickel.—This metal combines with oxygen in two proportions, forming a protoxide and a sesquioxide.

The *protoxide*, Ni.O., is prepared by precipitating a salt of nickel by caustic potash; a grass-green hydrated oxide of nickel separates, Ni.O.+H.O., which, when dry, gives the pure ash-gray oxide. This is the only oxide of nickel which forms salts. It is not, by itself, soluble in water of ammonia; but if a salt of nickel be decomposed by ammonia, the precipitate which first forms is dissolved on adding an excess of the alkali, forming a blue solution, in a great degree characteristic of this metal.

The *Peroxide of Nickel*, Ni_2O_3, is a black powder, prepared by boiling the protoxide in a solution of chloride of lime; the oxygen of the lime changes the protoxide into peroxide, 2Ni.O. and Ca.O.Cl. producing $Ni_2.O_3$ and Ca.Cl. When ignited, this oxide gives oxygen and protoxide; with muriatic acid it forms protochloride and chlorine. It does not form any true salts.

Nickel is easily recognised by its solutions giving with ammonia a green precipitate, which dissolves in an excess, forming a blue solution, and by giving with yellow prussiate of potash a white precipitate. The solutions of nickel are not precipitated by sulphuretted hydrogen, but give a black sulphuret of nickel with hydrosulphuret of ammonia.

The sulphuret, seleniuret, and phosphuret of nickel do not present any point of interest.

Of Cobalt.

The name of this metal has its origin in a still more singular circumstance than that of the preceding; from the bright metallic appearance of its ores, the miners of the Middle Ages were led to expect an abundant produce, but the modes of reduction then in use were employed without avail; it was hence imagined that these ores were especially protected by the guardian spirits of the mines, or Kobolds, and these minerals were termed *Die Kobold's erze, the Kobold's ores.* At a later period a peculiar metal was extracted from them, and as the older name had been corrupted into kobalt ore, the metal was called cobalt.

Cobalt exists in nature, combined with arsenic and with sulphur; it is universally associated with nickel, which it resembles so closely in its properties that the perfect separation of these two metals is one of the most difficult operations in analysis.

To obtain the cobalt, the native arseniuret is roasted in a current of air, so as to oxidize both metals, as described, p. 334. The residual impure oxide of cobalt is sold in commerce under the name of *Zaffre*. This zaffre is dissolved in muriatic acid, and treated with sulphuretted hydrogen, by which the copper and arsenic are separated. From the filtered liquor, the cobalt is thrown down by carbonate of potash, and then, to free it from oxide of iron, it is digested with oxalic acid, which dissolves the peroxide of iron, and leaves an insoluble oxalate of cobalt; this may still be contaminated with nickel, but for the details of the separation of these metals, I must refer to more extended works.

The oxalate of cobalt, when ignited, yields carbonic acid and metallic cobalt in a spongy form. Cobalt melts into a button more easily than cast iron; it is reddish-gray; specific gravity 8·5; when perfectly pure, it is not susceptible of becoming magnetic. It acts upon water and acids more rapidly than nickel, but much less actively than iron or zinc. The symbol of cobalt is Co., and its equivalent 369 or 29·6.

Oxides of Cobalt.—Cobalt combines with oxygen to form two well defined oxides, a protoxide and sesquioxide; there are also a complex oxide, and a compound of which the constitution is not well known, but which is probably a deutoxide.

Protoxide of Cobalt, Co.O., is prepared by adding caustic potash to a solution of a

salt of cobalt; a fine blue powder falls, which is a hydrate, Co.O. . H.O.; when deprived of its water, it becomes ash-gray: it is the only oxide of cobalt which forms salts with acids.

Sesquioxide of Cobalt, Co_2O_3, is prepared as the sesquioxide of nickel; it is a black powder, which, with hydrochloric acid, gives chlorine and protochloride: it does not form salts.

The complex oxide is $Co_3O_4 = Co.O. + Co_2O_3$, similar to the magnetic oxide of iron and red oxide of manganese.

Cobalt is recognised in solution by producing with water of ammonia a blue precipitate, which redissolves in an excess of the alkali, forming a liquor which is of a fine rose colour if the cobalt be pure, but brownish red if nickel be present; it is not precipitated by sulphuretted hydrogen, but is thrown down black by hydrosulphuret of ammonia. The most remarkable test for cobalt is its power of colouring glass blue. The most minute trace of this metal may be thus recognised before the blowpipe. It is, indeed, on this character that is founded the most important uses of cobalt in the arts; glass coloured deep blue by cobalt, and ground to an impalpable powder, constitutes the smalts used to give to writing paper and to linen a delicate shade of blue. The blue colours upon porcelain and delft are also produced by cobalt; when speaking of magnesia (p. 349) and alumina (p. 351), I have noticed the assistance given by cobalt in the detection of these earths before the blowpipe; alumina, coloured strongly blue by cobalt, is used in commerce as a pigment, cobalt blue, in place of ultramarine.

The blue colours of cobalt are spoiled if brought into contact with chlorine or oxygen, the black sesquioxide of cobalt being formed. If paper be blued by smalts without the bleaching liquor having been well washed out of the pulp, it is injured by acquiring a brown tinge; and by melting together cobalt-glass and black oxide of manganese, a deep black glass is formed, 2(Co.O.) and $Mn\,O_2$ giving Co_2O_3 and Mn.O.

The sulphuret and seleniuret of cobalt consist of an equivalent of each element, but do not require notice.

Of Zinc.

This metal is found in nature in considerable quantity, combined with sulphur, forming sulphuret of zinc, *zinc blende*; also as oxide of zinc, which, united with carbonic acid or with silicic acid, forms the two varieties of *calamine*. The reduction of the metal is effected from these ores respectively on the principles already described in Chapter XII., but, from the volatility of the metallic zinc, the process is carried on in crucibles or large earthen retorts in place of the open reverberatory furnace. In England the crucibles are closed above, but perforated at the bottom, so as to admit an iron tube to be fitted in, the top of which rises a little above the surface of the materials, and the bottom of which, passing through the floor of the furnace, opens just over the surface of a reservoir of water The zinc, when reduced, is converted into vapour, which escapes through the tube, condensing when it gets below the fire into a liquid metal, which, dropping into the water, solidifies. In Silesia very large earthen retorts are employed, not unlike those figured in page 289 for the preparation of German oil of vitriol.

The zinc of commerce, as thus obtained, is impure; it contains traces of carbon, iron, cadmium, and often arsenic. It may be freed from the fixed impurities by redistillation in an iron retort; and by

rejecting the portions which distil over first, and which contain the cadmium and arsenic, it may be obtained quite pure. It is owing to the presence of these foreign bodies that ordinary zinc dissolves so rapidly in dilute sulphuric acid, as explained in page 135. It is a brilliant bluish-white metal, of a very crystalline texture; its singular variations of tenacity are described in page 328. At 773° it melts, and at a full red heat is volatilized, its vapour burning in air with a splendid white flame, and forming clouds of oxide of zinc, so light as to have been called by the older chemists *lana philosophica* and *nihil album*. When exposed to the air, even in presence of water, zinc is not continuously oxidized. It becomes covered with a varnish of a gray substance, probably a definite suboxide, which is not farther altered by exposure, and hence this metal is admirably fitted for the various purposes of domestic and technical use to which it has recently been applied. In a galvanic circuit of two metals, zinc is almost always positive, and hence it preserves the other metal, even if it be iron, from oxidation. The actual corrosion is, however, in this case, not diminished, but rather augmented in amount; but, being concentrated solely upon the zinc, it is easy to arrange it so as to prevent injury. If zinc be quite pure, it is little acted upon by acids; all that is known of its relations in this respect has been already described in pages 198 and 248.

The symbol for zinc is Zn. Its equivalent number 403·2 or 32·3.

Oxide of Zinc. — Zn.O. Equivalent 503·2 or 40·3. Although there is some reason to suppose the existence of other oxides of zinc, yet at present we possess accurate knowledge only of the protoxide. This is formed when the metal is burned in air or oxygen. It is produced, also, when the zinc is oxidized by the decomposition of water, either at a red heat or assisted by an acid. To form the oxide by combustion, it is sufficient to project a small fragment of zinc into a crucible heated to bright redness, and slightly inclined, so that a current of air may pass through it. When the metal takes fire, another crucible is to be placed inverted over the first, but still allowing a certain access of air. The oxide of zinc being not really volatile, but only mechanically carried up by the current of air, is deposited on the inside of the upper crucible as a loose cottony mass, which, while very hot, is of a fine canary colour, but becomes pure white when completely cold.

Such is the tendency of oxide of zinc to enter into combination, that the precipitates given by the caustic alkalies in a solution of a salt of zinc are basic salts, and not the mere oxide. To prepare the oxide, a solution of sulphate of zinc is to be decomposed by carbonate of soda; the precipitate is carbonate of zinc; and by heating this to redness in a crucible, the carbonic acid passes off, and the oxide of zinc remains pure. This oxide is a powerful base; it neutralizes the strongest acids, and its salts are some of the most definite and characteristic that exist: they are easily recognised. In their solutions, the caustic alkalies all produce voluminous white precipitates, which are redissolved by an excess of the alkali. An alkaline carbonate gives a similar precipitate, which, however, is not redissolved by an excess, except it be carbonate of ammonia. Hydrosulphuret of ammonia produces a white precipitate of hydra

ted sulphuret of zinc, if the solution be not very acid. Sulphuretted hydrogen does so only if the solution be completely neutral A solution of zinc with much free acid is not affected by sulphuretted hydrogen, either free or combined.

The native *Sulphuret of Zinc*, Zn.S., is found in crystals of a variety of colours; it is a protosulphuret, and may be artificially formed by melting zinc and sulphur together. It is decomposed by acids, sulphuretted hydrogen being given off, and a salt of zinc produced.

Of Cadmium.

This metal exists but in small quantities in nature; the only ore of it is its sulphuret, a mineral but lately found, and still very rare; it accompanies almost universally, though in small quantities only, the ores of zinc, and is obtained in the working of zinc ores by taking advantage of its greater volatility. The details of its purification need not be inserted. It is white like tin; it is more fusible and more volatile than zinc; its specific gravity is 8·69; it dissolves very slowly in dilute sulphuric acid, but rapidly in dilute nitric acid; it combines with oxygen only in one proportion. Its symbol is Cd., and its equivalent 696·8 or 55·8.

The *Oxide of Cadmium*, Cd.O., equivalent 796·8 or 63·8, is obtained by processes exactly such as described for oxide of zinc. When anhydrous, it is an orange powder; its salts, which are very stable, resemble closely those of zinc, from which they are distinguished by giving with sulphuretted hydrogen a fine yellow precipitate, and with carbonate of ammonia a white precipitate, insoluble in an excess: its salts, like those of zinc, are all colourless.

Sulphuret of Cadmium, Cd.O., is found native near Greenock; it is yellow like orpiment, but is not volatile; it does not dissolve in water of ammonia nor of potash.

Of Tin.

This metal, from the ease with which it is extracted from its ores, has been known from the earliest ages, and in all countries, both of the East and West. Before the working of iron was discovered, cutting instruments of all kinds were made of an alloy of tin and copper (bronze), which in hardness was little inferior to steel; but, from its incapability of being tempered with the same exactness, was only an imperfect substitute for it. It was from the tin mines of Cornwall that England first became known to the then more civilized nation of Phœnicia. A great quantity of the tin of commerce is still obtained from that county; but, in addition, it is imported from Mexico and the East Indies. The tin ore has been found in Ireland (county Wicklow), but not as yet sought for with a view of extracting the metal from it.

The usual ore of tin is the native peroxide, which is found in veins, and also in fragments in the soil formed by the disintegration of the rocks. The process of reduction is the simplest possible, the ore being smelted with the fuel, as described p. 332. The metal thus obtained is still farther purified from any admixture of foreign metals by the process of *liquation*, which is founded on the easy fusibility of pure tin. The ingots, or pigs of tin, are gently heated until they begin to melt, and then the heat being prevented

from rising higher, the pure metal melts completely out, leaving behind the impurities combined with a proportion of tin, forming a mass of less commercial value. The tin thus purified is termed *grain tin;* the residual mass is called block tin. The former is known by presenting the appearance of a mass of irregular columns, like those formed by starch, or by basalt, as in the Giant's Causeway, and emitting, when bent, a peculiar creaking sound. The block tin possesses these characters in a very small degree, or not at all.

Tin, when pure, is white like silver, brilliant, and after gold, silver, and copper, the most malleable of the metals. It is very soft, may be bent easily, and has but little tenacity. Its specific gravity is 7·3. It is one of the most fusible of the metals, melting at 442° Fah. Tin oxidizes but very slowly in contact with air and water, and is hence used to protect the surface of the more easily oxidable metals, particularly copper, in household use. It dissolves but slowly in dilute muriatic acid, but rapidly if the acid be strong and boiling. Nitric acid acts with great energy on it when concentrated, forming the peroxide.

The symbol of tin is Sn., derived from its Latin name *stannum.* Its equivalent numbers are 735·3 or 58·9.

There are three oxides of tin, of which the first acts as a base, the second appears indifferent, and the third possesses acid properties.

Protoxide of Tin.—Sn.O. Equivalent 835·3 or 66·9. On adding water of ammonia to a solution of protochloride of tin, a copious white precipitate is obtained, which does not contain ammonia, but is the hydrated oxide, Sn.O. . H.O. The same precipitate is produced by an alkaline carbonate, the carbonic acid becoming free. When this white hydrate is heated in a retort filled with carbonic acid gas, it gives off its water, and the true protoxide of tin remains as a dense black powder.

If the hydrate be heated in the open air, it absorbs oxygen, and becomes peroxide; and if the black protoxide be touched when cold with a red-hot coal or wire, it inflames and burns like tinder, forming peroxide. The salts of tin may be formed by digesting the hydrated oxide in acids. It also dissolves in solutions of the caustic fixed alkalies, but after some time metallic tin is deposited, and a compound of the alkali with peroxide of tin remains dissolved, 2Sn.O. producing Sn. and $Sn.O_2$. This protoxide of tin is remarkable for its tendency to unite with more oxygen. Hence, by a solution of a protosalt of tin, the less oxidable metals are reduced from their solutions. In this way mercury, silver, gold, platina, may be thrown down in the metallic state, and iron and copper reduced from the higher to the lower degrees of oxidation.

The *Sesquioxide of Tin*, Sn_2O_3, is prepared by boiling peroxide of iron in a neutral solution of protochloride of tin. The sesquioxide of tin precipitates, and protochloride of iron dissolves, 2Sn.Cl. and Fe_2O_3 producing Sn_2O_3 and 2Fe.Cl. It is a gray powder; it absorbs oxygen readily, and appears to form salts, which have been, as yet, little examined.

Peroxide of Tin. Stannic Acid.—$Sn.O_2$. Equivalent 935·3 or 74·9. This substance is produced in all cases where tin is allowed to combine with oxygen freely. It exists in nature, constituting the common ore of tin (*tin stone*). It is most readily prepared artificially by pouring the liquid nitric acid, sp. gr. 1·42, on metallic tin, in

foil or powder; the action is very violent, and the metal is totally converted into a white powder, which is the hydrated peroxide. By ignition the water is given off, and the anhydrous oxide remains of a pale yellow colour.

If the perchloride of tin be decomposed by an alkali, a white precipitate of hydrated oxide is obtained, in appearance identical with that prepared by nitric acid, but so different in properties that Berzelius, and after him many chemists, look upon them as isomeric bodies. He calls that by nitric acid, α peroxide, and that from the perchloride, β peroxide, and their properties may be contrasted as follows:

The α modification is totally insoluble in nitric acid and in sulphuric acid, whether strong or dilute. It is insoluble in muriatic acid, but is changed by it into an in soluble basic salt.

The β modification dissolves while yet moist in dilute nitric and sulphuric acids very copiously, and the solution is permanent if some salt of ammonia be added to it. In muriatic acid it dissolves rapidly and copiously.

The two modifications of oxide of tin dissolve in solution of caustic potash, and, when again precipitated from it by an acid, retain their original properties. These modifications are also capable of being transformed into each other; the α into β by distillation with strong muriatic acid, and the β into α by boiling with nitric acid.

The hydrated peroxide of tin reddens litmus, and combines with alkalies to form salts, but not with acids, except in the β form. It is used in the arts as a polishing material under the name of *putty*, and in glass and enamelling, in order to give the milk whiteness used for dials of watches and other purposes.

There are three sulphurets of tin corresponding to the oxides.

The *Protosulphuret*, $Sn.S$, is precipitated as a brown powder from a solution of protochloride of tin on the addition of sulphuret of hydrogen. It thus serves for the detection of tin in that condition. The *Sesquisulphuret*, Sn_2S_3, is of no importance.

The Bisulphuret of Tin, $Sn.S_2$, equivalent 1137·6 or 91·1, may be prepared by decomposing a solution of perchloride of tin by sulphuretted hydrogen, which it precipitates of a golden yellow colour. This is a strong sulphur acid. It dissolves readily in solutions of the sulphurets of the alkaline metals, forming sulphur salts. If it be strongly heated, it abandons an atom of sulphur, and is converted into the protosulphuret. It may be also prepared in the dry way, and then possesses considerable interest as being one of those substances which, being obtained from the common metals, and simulating the appearance and some of the properties of gold, led the ancient alchemists to the belief of probable success in their attempts at transmutation. The bisulphuret of tin may be prepared in the dry way according to several processes, but to give it the peculiar lustre which obtained for it its name of *mosaic gold*, the following is the best though not the most simple: twelve parts of pure tin are to be melted with six parts of mercury, and rubbed up in a glass mortar with seven of flowers of sulphur and six of sal ammoniac. This mixture is to be placed in a glass flask, and heated in a sand-bath until no more fetid white vapours are given off. The heat is to be then raised to dull redness, sulphuret of mercury and chloride of tin sublime, and the mosaic gold remains in the bottom of the vessel in metallic-looking scales of a brilliant gold colour. The use of the mercury in this process is to facilitate the combination of the tin and sulphur, and the sal ammoniac seems by its evaporation to prevent the temperature becoming so high as to decompose the bisulphuret.

The seleniurets and phosphurets of tin are not known.

Tin is easily recognised in solution by the action of hydrosulphuret of ammonia, which produces with solutions of the peroxide a golden yellow, and in solutions of the protoxide a brown precipitate. These both dissolve in an excess of the precipitant. The protoxide of tin is also known by its power of reducing the salts of gold, silver, and mercury to the metallic state.

Of Chromium, or Chrome.

This metal derives its name from the variety and brilliancy of the colours of its compounds (Χρωμος). It exists as chromic acid combined with lead or with copper in some rare minerals, but abundant-

ly as chromic oxide in the chrome-iron ore ($Fe.O.+Cr_2O_3$). It is from this source that all the preparations of chrome are obtained indirectly, but that ore being treated upon the large scale for the manufacture of chromate of potash, it is this salt, as found in commerce, that may be looked upon as the source of chrome for all other purposes. The metal is obtained by mixing the oxide with lampblack and oil, and exposing it to an intense heat in a crucible lined with charcoal. It is a grayish-white metal, very infusible, brittle, not magnetic, and sp. gr. 5·9 or 6·0. It is not attacked by dilute sulphuric or muriatic acids, but dissolves in hydrofluoric acid with evolution of hydrogen gas.

Chrome combines with oxygen in two proportions, forming an oxide and an acid. Its symbol is Cr., and its equivalent numbers are 351·8 or 28·19.

Oxide of Chrome, Cr_2O_3, equivalent 1003·6 or 80·4, may be obtained by a great variety of processes. Thus, if chromate of mercury be heated to redness, the oxide of mercury and half the oxygen of the chromic acid are expelled, and the chromic oxide remains of a beautiful green colour.

If bichromate of potash be mixed with sal ammoniac and heated to redness, chloride of potassium, water, nitrogen, and oxide of chrome result, and the latter is obtained pure by washing the residual mass with boiling water. In this process, $2Cr.O_3+K.O.$ and $Cl.N.H_4$ produce K.Cl., N., 4H.O., and Cr_2O_3. The oxide so obtained is pulverulent, but it may be obtained crystallized as follows: the vapour of a compound which will be hereafter described, chlorochromic acid, is to be passed through a tube of hard glass, kept at a full red heat, oxygen and chlorine gases are given off, and oxide of chrome is deposited on the inside of the tube in rhombic octohedrons, isomorphous with those found native of alumina (corundum) and peroxide of iron; the chlorochromic acid, $2(Cr.O_2Cl.)$ giving off 2Cl. and O., and Cr_2O_3 remaining.

This oxide of chrome is the basis of an extensive class of salts, and it may also be obtained by precipitation from any solution containing it. Its salts are generally made from the bichromate of potash of commerce, by the addition of some deoxidating agent and the necessary acid. Thus, to form sulphate of chrome, a solution of bichromate of potash is warmed, and treated successively with sulphuric acid and alcohol, until its orange colour is changed into deep green. The liquor then contains the double sulphate of chrome and potash (chrome alum), and from it the oxide may be precipitated on the addition of an alkali, as a pale green hydrate. In this condition, the oxide of chrome dissolves readily in acids, and also in solutions of the fixed caustic alkalies, but scarcely in ammonia, resembling very closely, in all these characters, alumina. Its solutions are either green or purple, and it is probable that this difference is due to more than a mere difference in the degree of concentration. When the hydrated oxide is heated nearly to redness, it suddenly begins to glow like tinder, giving off its water, and losing its solubility in acids, except they be hot and concentrated. It is remarkable that sulphate of chrome, made from the ignited oxide, will not combine with sulphate of potash to form a chrome alum.

Chromic Acid.—$Cr.O_3$. Equivalent 651·8 or 52·2. To prepare this acid, a solution of bichromate of potash is to be treated by hydrofluosilicic acid gas, until the potash has been precipitated completely. The resulting liquor is to be cautiously evaporated to dry-

ness, and then redissolved in a small quantity of water. The solution is of a dark brownish-red, and when evaporated again gives the dry chromic acid. It may be obtained in a beautiful form, though not in quantity, by decomposing the vapour of the perfluoride of chrome by a moistened slip of paper. $Cr.F_3$ and $3H.O.$ produce 3 $H.F.$ and $Cr.O_3$, which last is deposited on the surface of the paper in crimson scales and needles of great brilliancy. This acid, when heated strongly, gives up half its oxygen, being reduced to the state of oxide. It combines with bases, forming several important classes of salts, in which it is isomorphous with the sulphuric and manganic acids. Its salts are all coloured, generally yellow, orange, or red. They will be described in another chapter.

Chromium is characterized by the remarkable colours of its compounds when dissolved, and by giving, when in the state of oxide, a green precipitate with the alkalies. In the state of acid, it is known by producing, with the salts of lead, a yellow, and with the salts of the black oxide of mercury, an orange precipitate. It is at once recognised by the beautiful green colour which it communicates to glass. It is, on this account, extensively used in staining glass and painting on porcelain, and a number of its salts are employed as pigments and as dyes.

By the action of deoxidizing agents, or sulphurous acid or sugar, upon bichromate of potash, a brown substance is generated, concerning the nature of which opinion is very much unsettled. There is reason to suspect the existence of a peroxide of chrome, $Cr.O_2$, which this matter may possibly be. When it is washed with much water, or digested in alkaline liquors, chromic acid is dissolved out and oxide of chrome remains, $Cr_2O_3+Cr.O_3=3Cr.O_2$.

The sulphurets, seleniurets, and phosphurets of chrome are not important.

Of Vanadium.

This metal, of recent discovery, derives its name from Vanadis, a deity of Scandinavian mythology. It is found native as vanadic acid, in a very rare mineral, vanadiate of lead, but is of so little importance that a slight notice of it will suffice, although it forms a great variety of combinations, which resemble very remarkably those of manganese and chrome. The metal itself has been obtained, but of its properties nothing positive is known. Its symbol is V.; its equivalent numbers are 856·9 or 68·7.

The Protoxide of Vanadium, V.O., is a black powder, formed by acting on vanadic acid at a red heat with hydrogen gas. It combines with acids, forming salts which resemble probably those of the protoxide of manganese. When heated in the air, it absorbs oxygen and becomes *vanadic oxide*, $V.O_2$, which is a base combining with acids and forming salts which are generally blue. It acts also as an acid, forming crystallizable salts with the fixed alkalies.

The *Vanadic Acid*, $V.O_3$, resembles very much the chromic and manganic acids. It is a red powder, which may be melted at a red heat without losing oxygen. It is very slightly soluble in water. It forms various classes of salts, of which some are white, some yellow, and others orange red. In these characters it resembles the chromic acid, but it is distinguished from chrome by producing, when deoxidized, a blue solution, while that from chrome is green.

SECTION IV.

METALS OF THE FOURTH CLASS.

Tungsten and Molybdenum.

Tungsten.—This metal exists, combined with oxygen, as tungstic acid, in the native tungstates of lime and iron; by boiling the tungstate of lime in strong muriatic acid, the lime is dissolved out, and tungstic acid remains as a yellow powder, which may be farther purified by solution in water of ammonia, and igniting the

tungstate of ammonia. It is a deep yellow powder, which forms well-defined crystallizable salts with the alkalies. The symbol of tungsten is W., from its German name *Wolfram*, and its equivalents 1183 or 94·8. The tungstic acid resembles the chromic acid, being $W.O_3$. When this acid is exposed to a current of hydrogen gas at a temperature about dull redness, it loses one third of its oxygen, and forms *tungstic oxide*, $W.O_2$, of a copper-red colour. This may be also formed by diffusing tungstic acid through dilute muriatic acid in which a slip of zinc is immersed; the nascent hydrogen then effects the deoxidation. At a full red heat, hydrogen reduces tungsten to the metallic state, removing all the oxygen. The metal is like iron in appearance, and very heavy, its sp. gr. being about 17·5.

The most curious fact in the history of tungsten is its producing a substance having an extraordinary similarity to gold. It is prepared by adding to fused tungstate of soda as much tungstic acid as it will dissolve, and exposing the product at a full red heat to a current of hydrogen gas; the residual tungstate of soda is then to be dissolved out. The new compound, which consists of tungstic oxide united to soda, $Na.O.+2W.O_2$, remains in scales and cubes of a splendid gold colour. It resists the action of acids and alkalies, even of aqua regia, in which gold dissolves, and only yields to strong hydrofluoric acid. Had it been discovered at an earlier period in science, it might have lent exceedingly plausible support to the belief in transmutation. It is the more curious, as it cannot be formed by directly combining soda with tungstic oxide, which, indeed, appears unable to unite either with alkalies or acids.

There exist two sulphurets of tungsten, $W.S_2$ and $W.S_3$, of which the latter is the most interesting. It is formed by dissolving tungstic acid in hydrosulphuret of ammonia, and precipitating by an acid. It is a blackish-brown powder, and one of the strongest sulphur acids. Many of its compounds with the sulphurets of the alkaline metals may be crystallized.

Molybdenum.—This metal exists combined with sulphur, and also with oxygen, as molybdic acid, in some minerals. It is not of any considerable interest. When obtained in the metallic state it is white, sp. gr. 8·6, acted on only by concentrated nitric and sulphuric acids, and by aqua regia. Its symbol is Mo. Its equivalent 598·5 or 47·9. It combines with oxygen in three proportions.

Molybdic Acid, $Mo.O_3$, is easily prepared by roasting the native sulphuret of molybdenum; the sulphur burns out as sulphurous acid gas, and the molybdenum, absorbing oxygen, remains as molybdic acid. This may be purified as described for tungstic acid. Molybdic acid prepared at a low temperature is white, but becomes yellow when fused at a red heat. It is sparingly soluble in water. It dissolves in alkaline liquors, forming salts which are neutral and crystallizable.

Molybdic Oxide, $Mo.O_2$, is best prepared by mixing together molybdate of soda and sal ammoniac in a crucible, and igniting the mass rapidly. When the product is washed with water, a dark brown powder is obtained, which is molybdic oxide. This oxide appears to form salts with both acids or alkalies, of which some may be crystallized. A molybdate of molybdenum, or, rather, a complex oxide, also exists, $Mo.O_2+2Mo.O_3=Mo_3O_8$. It is a blue powder.

When a solution of molybdate is decomposed by as much muriatic acid as redissolves the molybdic acid, which is at first thrown down, and a slip of zinc is immersed in the liquor, the hydrogen evolved deoxidizes the molybdic acid, and a precipitate is formed upon the zinc, at first blue, then brown, and finally black; thus passing through all the intermediate degrees to the last, the *Molybdous Oxide*, Mo.O. This is a very feeble base, forming with acids salts which do not crystallize.

Sulphur combines with molybdenum in three proportions, forming $Mo.S_2$, $Mo.S_3$, and $Mo.S_4$. Of these the bisulphuret, $Mo.S_2$, is important, as being the native ore from which the metal and its compounds are generally prepared. It is a soft gray substance, so like black lead as to have been mistaken for it until its nature was pointed out by Scheele. All these sulphurets are sulphur acids, and form salts.

Of Osmium.

This metal exists in nature alloyed with iridium, and accompanies the ores of platinum. The methods of its extraction from these ores are so complex and circuitous that I shall not introduce them here. In the systematic works, a complete account of the processes pursued will be found.

The most interesting property of osmium is its forming a highly volatile oxide of an exceedingly penetrating odour, whence the name (οσμη). When this is dissolved in muriatic acid, and placed in contact with mercury, the osmium is reduced, and by distilling off the mercury it is obtained as a black powder; but by heat and compression it may be rendered coherent, and of a brilliant white colour. In the state of powder, osmium burns when heated to redness in the air, and is oxidized by nitric

acid, but loses both these characters when ignited. The symbol of osmium is Os. Its equivalent is 1244·5 or 99·7. It combines with oxygen in three proportions.

The *Osmic Acid*, or *Peroxide of Osmium*, $Os.O_4$, is always formed when osmium is burned in air or in oxygen gas. It condenses in long white needles. Its odour is remarkably acid and pungent. It melts at 212°, and boils at a heat little higher. It is soluble in water. The solution has no action on vegetable colours, but it combines with the alkalies, forming *osmiates*.

The *Osmic Oxide*, *Deutoxide of Osmium*, $Os.O_2$, is produced by the decomposition of a solution of osmiate of ammonia, by a temperature of 150°; nitrogen gas is given off, and a brown powder is deposited.

The *Protoxide of Osmium* is produced by decomposing a solution of protochloride of osmium by potash; a deep green, almost black, powder is thrown down, in which the oxide is combined with water and traces of the alkali.

The sulphurets of osmium are not known.

Columbium, or Tantalum.

This metal was discovered first in an American mineral, from whence its name; it was subsequently, but independently, discovered in some very rare Swedish minerals, and from the difficulty of its extraction, the name tantalum was given to it, which it still bears upon the Continent, and from whence its symbol is Ta. The process required to prepare it need not be described, as it is similar to that for obtaining silicon.

Metallic Columbium, or Tantalum, is a black powder, which, when burnished, appears iron gray. No acid but the hydrofluoric appears to have any action on it. It takes fire when heated in the air, and burns vividly. Its equivalent numbers are 230·7 or 185. It combines with oxygen in two proportions.

Tantalic, or Columbic Acid, $Ta.O_3$, exists native in all the minerals containing the metal. To procure it, the mineral is fused with carbonate of potash, and the tantalate of potash, which is soluble, is to be decomposed by muriatic acid. The tantalic acid precipitates as a white powder, which contains water, and reddens litmus paper. When tantalic acid is heated strongly in a crucible with charcoal, but a slight film of it is reduced to the metallic state, the great mass being brought only to the state of *tantalic oxide*, $Ta.O_2$. This substance is gray. It is insoluble in all acids.

The similarity of tantalum to silicon is very great; it resembles it in forming, with fluorine and potassium, a double fluoride, from which the metal is obtained.

Titanium.

This metal, although not met with in large quantities, is yet found in a great variety of minerals. It is not found native in a metallic state, but combined with oxygen, forming titantic acid. To obtain metallic titanium, the volatile perchloride is employed. This body absorbs ammonia, forming a white substance, $Ti.Cl_2+2N.H_3$, which, when heated to redness, gives metallic titanium, with sal ammoniac and nitrogen, the hydrogen carrying off the chlorine. It is of a bright copper colour, almost perfectly infusible. Titanium exists in most of the clay iron stone, and hence, being reduced during the smelting of the iron, is found in the slags, crystallized in cubes of excessive hardness and brilliancy, sp. gr. 5·3. This metal is not acted upon by any acid except a mixture of nitric acid with hydrofluoric acid, and is oxidized, but very slowly, by melted nitre. It is perfectly unalterable by air or water. Its symbol is Ti. Its equivalent numbers are 303·7 or 24·3, and it combines with oxygen in two proportions.

Titanic Acid, $Ti.O_2$, exists native, constituting the mineral *rutile*, isomorphous with *tin stone* ($Sn.O_2$), and also in the mineral *anatase*. More abundantly it is found in the *titanic iron*, ilmenite, the formula of which is $Fe.O\,.\,Ti.O_2$, and, which is very remarkable, from having the same crystalline form as peroxide of iron, Fe_2O_3, so that the titanium would appear to replace the second atom of iron, and the formula to be $Fe.Ti.+O_3$. This is merely speculative, however, as iron is never isomorphous with tin, and in no other case with titanium, and I hence consider this instance as one of the coincidences of form described in pages 221 and 226.

Titanic acid is artificially prepared from the titanate of iron by igniting it with sulphur. The oxide of iron and sulphur form sulphurous acid and sulphuret of iron, and when this last is dissolved out by muriatic acid, the titanic acid remains behind. It requires other processes to render it absolutely pure, which need not be described here. It is a pure white powder, resembling silica very remarkably in its properties, and, like it, having a soluble and an insoluble modification. It is remark-

ably characterized by its solution in muriatic acid, giving with tincture of galls an orange precipitate, and by the immersion of a slip of zinc a fine purple powder, which is *Oxide of Titanium*, Ti.O.; the second atom of oxygen being removed from the acid by the nascent hydrogen. This oxide of titanium may also be procured by igniting titanic acid with charcoal; it is then a black powder, insoluble in all acids.

The *Bisulphuret of Titanium*, Ti.S_2, is a strong sulphur acid, but not otherwise important.

Of Arsenic.

This metal exists in nature in a great variety of forms, and in considerable quantity. It is found native, but more generally combined with other metals, as nickel, cobalt, iron; being considered, like oxygen and sulphur, as a *mineralizer* of other metals. Combined with sulphur, it constitutes the native orpiment and realgar; and with oxygen, as arsenic acid, it is united with metallic oxides in the native arseniates of lime, of iron, of lead, &c. The great proportion of the arsenic of commerce is obtained in the roasting of the cobalt and nickel ores, as described in p. 334. The current of hot air which has passed over the ignited ore carries with it, into a series of large chambers, the volatile arsenious acid, which is deposited under the form of a fine grayish powder on the walls and floor. This is discoloured by some of the oxide of the fixed metals, which is carried over mechanically by the draught, and it is, therefore, resublimed in iron vessels, the covers of which are allowed to become so hot that the arsenious acid, in condensing, shall aggregate itself into a vitreous mass, in which state it is sent into commerce.

The metallic arsenic may be prepared from the arsenious acid in many ways, but best by mixture with three times its weight of black flux (p. 334) in a crucible or earthenware retort, which is then to be heated to redness. If a crucible be used, another cold crucible, somewhat larger, must be inverted over it, on the inside of which the metal condenses, but with a retort it is deposited in the neck as an irregular mass of rhombohedrons, variously modified. It is very brittle; its sp. gr. 5·96. It sublimes at 356° F. without previously melting. The sp. gr. of its vapour is 10362. Its vapour, if in contact with the air, has a very characteristic garlic odour; which, however, belongs not to the pure metal, but to an oxide produced by a low degree of combustion which occurs. In the air it gradually absorbs oxygen, and falls into gray powder (*suboxide, fly powder*). By nitric acid it is rapidly oxidized, and deflagrates violently in melted nitre. In fine powder it burns spontaneously in chlorine gas, with a brilliant white flame, and burns similarly when heated in oxygen gas. The symbol of arsenic is As., and its equivalent numbers are 940·1 or 75·34.

Arsenic combines with oxygen in three proportions, forming a *suboxide*, of which the composition is not known. Many chemists look upon it as a mere mixture of metal and arsenious acid, for when it is heated it separates into these bodies. The other degrees of oxidation, the arsenious acid and arsenic acid, are of great importance.

Arsenious Acid. White Arsenic. Oxide of Arsenic—As.O_3, equivalent 1240·1 or 99·34—is found in commerce in masses, which, if recently sublimed, are perfectly colourless and transparent, but

gradually become milk-white and opaque. In general, the outer portions of the commercial masses have thus changed, while the interior retains its original transparency. This alteration is probably connected with the dimorphism of arsenious acid (p. 228), for the acid in these conditions differs in density and in solubility. The transparent is sp. gr. 3·74, and 100 parts of boiling water dissolve 9·68 parts of it; but the opaque acid is of sp. gr. 3·69, and 11·47 of it are soluble in 100 parts of boiling water. A solution of the vitreous acid reddens litmus paper, but that of the opaque acid restores, though feebly, the blue colour of litmus paper already reddened by an acid. The taste of arsenious acid is not marked, but rather slightly sweet: it leaves upon the palate, however, an acrid sensation.

The arsenious acid sublimes at 380° F. without previously melting. Its vapour is of sp. gr. 13670, being produced by

One volume of vapour of arsenic	=10362·0
Three volumes of oxygen . .	= 3307·8
the four volumes forming one . .	=13669·8

If it be very slowly sublimed, it condenses in regular octohedrons of exceeding brilliancy. It is, however, sometimes found, in the roasting of its ores, in crystals belonging to a different system (the rhombohedral). Arsenious acid is dissolved by liquid muriatic acid in large quantity, but crystallizes from that solution in octohedrons. If the opaque acid had been employed, the crystallization is not peculiar; but if it had been the transparent variety, the deposition of every crystal is accompanied by a sudden flash of light, very brilliant in the dark. The crystals so produced belong to the opaque kind, so that it would appear as if, at the moment of deposition, the particles changed their mode of arrangement, so as to pass from the transparent to the opaque dimorphous form, and that the alteration in molecular constitution occasioned the evolution of light, and probably of heat and electricity.

The arsenious acid combines with bases to form salts, which are, however, of such unstable constitution that they are but little known. It is particularly of importance from its highly poisonous properties, and from its being, more frequently than any other substance, administered to produce death. Its recognition is, therefore, to the medical chemist, one of the most important problems in analysis, and will be fully discussed when the other combinations of arsenic have been described.

Arsenic Acid.—$As.O_5$. Equivalent 1440·1 or 115·34. To obtain this acid, eight parts of arsenious acid are to be placed in a retort with two parts of strong muriatic acid, and boiled, while twenty-four parts of dilute nitric acid, of sp. gr. 1·25, are to be added in small quantities at a time. The mixture is to be distilled in a retort to the consistence of a sirup, and then transferred to a platina dish, in which it is to be evaporated to perfect dryness, and heated until all traces of nitric acid are expelled. The residual mass is milk-white, but anhydrous arsenic acid. The heat should not be raised to near redness, for then the arsenic acid is decomposed into arsenious acid and free oxygen. The mass thus obtained dissolves

but slowly in water, but ultimately the solution is complete; the arsenic acid has even so much affinity for water as to deliquesce rapidly in vessels which are not kept carefully closed.

The arsenic acid reddens litmus paper strongly, and forms with the alkalies perfectly neutral salts. At a high temperature it is capable of expelling all the volatile acids, even the sulphuric acid, from their combinations. In its compounds it resembles very closely the phosphoric acid; but it appears capable of forming only one of the three classes of salts which phosphoric acid produces. The arseniates are all tribasic, but as the quantity of fixed base varies, there are some neutral and others acid arseniates; the latter were formerly called binarseniates. Thus there are,

$3Na.O.+As.O_5+24$ aq.	called subarseniate of soda,
$2Na.O..H.O.+As.O_5+14$ aq.	" neutral arseniate of soda,
$Na.O..2H.O.+As.O_5+2$ aq.	" binarseniate of soda;

but the quantity of base is really constant, being in each three atoms, made up partly of water and partly of soda.

The arsenic acid is recognised by being precipitated golden yellow by sulphuretted hydrogen. The precipitate dissolves instantly in ammonia, and even in an excess of sulphuret of hydrogen; so that it may not be visibly produced, if the quantity of arsenic be small, until the liquid shall have been well boiled. A solution of any arseniate gives with nitrate of silver a brick-red powder, arseniate of silver, $3Ag.O.+As.O_5$, the formation of which is easily explained. An insoluble arseniate heated in a glass tube with charcoal powder gives a sublimate of metallic arsenic.

Arseniuret of Hydrogen.—It has been supposed, that when metallic arsenic is used as the negative electrode of a voltaic battery, the hydrogen evolved combines with it, and forms a brown powder, *hydruret of arsenic.* The same body was supposed to be generated in other ways; but it is now known that this substance is only metallic arsenic finely divided, and that there is but one compound of arsenic and hydrogen, the gaseous arseniuret of hydrogen. $As.H_3$.

This compound is easily obtained whenever nascent hydrogen comes into contact with metallic arsenic: thus, when an alloy of equal parts of zinc and arsenic is dissolved in dilute sulphuric acid, the hydrogen evolved combines with the arsenic, $3(S.O_3+H.O.)$ and $Zn_3As.$ producing $3(S.O_3+Zn.O.)$ and $H_3As.$ It is still more easily prepared by adding muriatic acid to a solution of arsenious acid in water, and immersing therein a piece of zinc; the hydrogen first evolved reduces the arsenious acid, and the metal is then separated as a fine brown powder, with which the hydrogen next evolved combines. This gas is generally stated to have a very disagreeable odour, which, however, I have not found it to possess. It is excessively poisonous; it burns with a brilliant white flame, water being formed, and arsenious acid or metallic arsenic being deposited according to the supply of oxygen to the gas; it is not absorbed by water; its specific gravity is 2694, formed by

One volume of arsenic vapour . .	$=10362\ 0$
Six volumes of hydrogen $68 \cdot 8 \times 6$.	$= 412 \cdot 8$
The seven being condensed to four .	$10774 \cdot 8$
Of which one weighs	$2693 \cdot 7$

Arseniuret of hydrogen decomposes most metallic solutions, precipitating metallic arseniurets of corresponding constitution ($R_3As.$). If a current of it be passed over chloride of copper, heated to about 400°, it is decomposed, $H_3As.$ and $3Cu.Cl.$ giving $Cu_3As.$ and $3H.Cl.$ This gas is absorbed by dry sulphate of copper, which it decomposes, water being evolved, and a blackish compound of sulphuric acid and arseniuret of copper being produced. This property is made available in the medico-legal examination of substances containing arsenic. If a fragment of chloride of mercury be heated in this gas, it is rapidly decomposed, muriatic acid gas and arseniuret of mercury being formed. At a full red heat the gas is decomposed completely by itself, so that if a single point of a tube, through which it streams, be ignited, all the arsenic is deposited a little beyond that point, in the metallic state, and only pure hydrogen passes on.

Sulphur and arsenic combine in several proportions: the *Bisulphuret of Arsenic*, $As.S_2$, exists native, forming the mineral *realgar*. It is prepared by fusing the following sulphuret with metallic arsenic, and subliming the product. It is a ruby-red crystalline mass; when it is digested in solution of caustic potash, a blackish powder remains, which may be looked upon as a subsulphuret; its definite nature is problematical. The *Tersulphuret of Arsenic*, $As.S_3$, *yellow arsenic*, *orpiment*, is found native, and may be easily prepared by decomposing a solution of arsenious acid with sulphuret of hydrogen, $As.O_3$ and $3H.S.$ giving $As.S_3$ and $3H.O.$ It is a rich yellow powder; when heated, it melts; and in close vessels sublimes unaltered, but otherwise it burns, partly forming arsenious and sulphurous acids; it is not quite insoluble in water. It is insoluble in acids, and best precipitated from an acid liquor. It is a strong sulphur acid, combining with the sulphur bases to form salts, *sulpho-arsenites*. It hence dissolves readily in hydrosulphuret of ammonia, and also in the caustic alkalies. In the last case there exists in solution an ordinary arsenite besides the sulphur salt; for, using potash, $2As.S_3$ and $6K.O.$ produce ($As.S_3+3K.S.$) and ($As.O_3+3K.O.$). When sulphuret of arsenic is ignited with black flux, metallic arsenic sublimes; and the separation of the metal is still more elegantly effected by heating the sulphuret, mixed with carbonate of potash, in a current of dry hydrogen gas.

The *Persulphuret of Arsenic*, $As.S_5$, corresponds to the arsenic acid, and is prepared by decomposing a solution of it, or of any of its salts, by sulphuretted hydrogen. It is yellow, paler than orpiment; sublimes without alteration in close vessels; is a strong sulphuric acid, and hence dissolves in solutions of the alkaline hydrosulphurets, forming *sulpho-arseniates;* the metal may be eliminated from it by the same means as those described for orpiment.

A substance sold in this country for killing flies, under the name of *king's yellow*, is, or ought to be, orpiment. The best sort is made by boiling together lime, sulphur, and white arsenic; but much of it consists merely of white arsenic coloured by some sulphur mixed with it. From the facility with which it may be obtained, and the manner in which it is left exposed, it is very frequently the source of fatal accidents.

Notwithstanding the scientific importance which arsenic possesses from the number and variety of its compounds, it is of much higher interest in consequence of the frequent necessity for the detection of excessively minute traces of it in cases of suspected poisoning, where a responsibility, involving the life of a fellow-creature, rests on the skill and accuracy of the medical chemist. The detection of arsenic under all possible circumstances is an object, therefore, to which all the powers of analysis should be brought to bear, and the methods at our disposal appear, if properly applied, to be satisfactory and complete. In a question so grave as this, no colours of precipitates, however so marked—no arrangement of mere results by test, no matter how corroborative, should be considered as by themselves decisive; the object of the chemist should be, the isolation and production of the metallic arsenic; and where this has not been done, it is certain that either there is no arsenic present, or that the skill of the operator cannot be absolutely relied on.

In poisoning by arsenic, the substance used is almost universally arsenious acid. To this, therefore, I shall confine my remarks at present; I shall afterward notice the peculiarities of its other preparations.

The arsenious acid being a very heavy powder, and but sparingly soluble, it is very rapidly deposited from any liquid through which it might have been diffused, and hence the vessels in which food had been contained should be carefully examined for any traces of it which might remain. This should not be omitted, even though they might appear to have been subsequently rinsed. Any substances vomited by the person suspected to be poisoned should be carefully examined for the same object; and in case of death, the materials in the stomach and its mucous surface must be similarly searched. The little grains of arsenious acid adherent to the surface of the stomach are frequently tinged yellow at the surface by sulphuretted hydrogen, if the examination be deferred until some time after death.

In case of such traces of white powder being found, the examination is very simple. Their porperties are:

1st. Heated alone in a glass tube, the powder sublimes and condenses in minute brilliant octohedrons.

2d. Mixed, in a tube closed at one end, with a little black flux, and ignited, metallic arsenic sublimes, forming a steel-gray crust, brilliant on the side next the tube, but dull and crystalline on the inside. On applying the nose to the open end of the tube and inspiring, a garlic odour is perceived.

3d. On cutting off the sealed end of the tube, and then heating the part containing the metallic crust, the tube being slightly inclined, the metal disappears, and a crust of white arsenic condenses a little higher up. A current of air passes through the tube, with the oxygen of which the metal combines. In this process the garlic smell becomes more marked than in No. 2.

4th. The white powder dissolves in water. It yields precipitates with the following reagents:

A. *Sulphuretted Hydrogen.*—A rich yellow: soluble in ammonia, and precipitated on the addition of an acid. This precipitate is *orpiment.*

B. *Ammonia-nitrate of Silver.*—A canary yellow; *arsenite of silver.* This reagent is very delicate, but the precipitate is soluble both in acids and ammonia, so that an excess of either must be avoided.

C. *Ammonia-sulphate of Copper.*—A fine apple-green. This is redissolved also by an excess of acid or of ammonia.

Each of these liquid reagents is liable to fallacy, which must be guarded against.

A. *Sulphuretted Hydrogen* gives precipitates more or less resembling that from arsenic with the following metals:

Cadmium.	Antimony.
Tin (persalts).	Iron (persalts).

The precipitate from cadmium is not soluble in water of ammonia.

The precipitate from tin, when dried and ignited with black flux, gives no sublimate of metal.

The precipitate of antimony acts in the same way as tin, but also it dissolves in strong muriatic acid, and the solution, diluted with much water, gives a white precipitate. The sulphuret of antimony is much more orange-coloured than that of arsenic.

The precipitate from a persalt of iron is pure sulphur; heated, it melts and burns completely away, without forming any solid product.

B. *Ammonia-nitrate of Silver.*—Phosphate of soda produces a yellow precipitate of tribasic phosphate of silver, exactly resembling the arsenite. It is, however, much more soluble in ammonia. They are at once distinguished by being collected and ignited. The arsenite gives off oxygen and arsenious acid, while metallic silver remains; but the phosphate gives no volatile product.

C. The *Ammonia-sulphate of Copper* is uncertain, unless it be dried and reduced; for there are numerous basic compounds of copper, which resemble it very much in colour.

None of these liquid reagents are, therefore, in themselves positive, unless by extraction of the metal; and this is the more important when the operator has to work, not with the clear solutions prepared intentionally for illustration, but with the complex and discoloured liquids obtained from the stomach and intestines.

The process to be then followed may be either of two kinds; the first consists in converting the arsenic into sulphuret, the second into arseniuret of hydrogen. I will describe each in their turn.

The contents of the stomach and small intestines, or the matter ejected by vomiting during life, are to be boiled in distilled water for half an hour, and then the liquor strained through a linen cloth. If it be too thick or coloured to allow of a small quantity of precipitate being observed and separated, a current of chlorine gas is to be passed through it, by which most of the animal matter dissolved is coagulated, and a more convenient solution obtained. This being strained or filtered, is to be well boiled to expel the excess of chlorine, and then submitted to the action of a current of sulphuretted hydrogen gas. The animal matters may also be removed from the solution by rendering it acid by nitric acid, and then adding an excess of nitrate of silver. When the precipitate which forms has been separated, the excess of silver is to be thrown down by some

common salt, and the liquor being then filtered, is fit for the action of the sulphuretted hydrogen.

When the liquor smells strongly of this gas, there has been enough passed through, and it is then to be boiled briskly for a few minutes to expel the excess, and favour the deposition of the precipitate produced. This is to be then collected on a filter, washed carefully with water acidulated by muriatic acid, and dried at a moderate heat.

When completely dry, it is to be mixed with about twice its bulk of black flux, and ignited in a small tube of hard glass closed at one end. In introducing the materials, care must be taken not to soil the sides of the tube; metallic arsenic sublimes, which is recognised by the characters given already in pages 376, 380.

The process by arseniuretted hydrogen was first proposed by Mr Marsh, and has been found of surprising delicacy and exactness; the liquid having been freed from animal matters, and obtained as thin a fluid as possible by either of the processes, by chlorine or nitrate of silver, already described, it is rendered moderately acid by muriatic or sulphuric acid, and introduced into a flask or bottle, to the neck of which is adapted a narrow tube of hard glass, which, after passing horizontally for a few inches, turns up and forms a jet; a piece of zinc being introduced into the acid liquor, hydrogen is evolved, which combines with any arsenic that may be present, and, forming the gaseous arseniuret of hydrogen, passes off. When the gas issuing from the jet is set on fire, if the hydrogen be pure, no other product is generated but water; but if a slight trace of arsenic be present, the flame is whitish, and on holding over the jet a fragment of glass or porcelain, or a film of mica, a deposite is produced, which may be white from arsenious acid, or brown from metallic arsenic, according to the height at which the plate is held, and the consequent completeness of the combustion, or the reverse. If the quantity of arsenic be too small to produce this effect in a certain time, it may be better detected by igniting a portion of the horizontal arm of the tube. All the arseniuretted hydrogen, in passing that point, deposites its arsenic, which is carried a little beyond the heated portion by the current, and condenses there as a distinct metallic film; as the tube may be kept thus red-hot for some hours, the smallest trace of arsenic may be thus concentrated on a single point, and its properties accurately verified.

Where the liquor is still thickish from dissolved organic matter, the gas bubbles would not break rapidly, but form a froth, which, passing into the tube, would prevent altogether the successful employment of the methods just described. In this case the liquid should be made so feebly acid as that the gas shall be generated but very slowly, and that there shall be but little hydrogen in excess. The tube, in place of terminating in a jet, is to be bent down so that it shall pass under the edge of a jar in the pneumatic trough, and, the apparatus being so left for any length of time, the gas evolved may be collected and subsequently examined. Or, what is perhaps still better, the tube may dip under the surface of a dilute solution of nitrate of silver or of sulphate of copper, and all the arseniuretted hydrogen being then absorbed and decomposed, metallic

arseniurets are produced, which easily yield, by the application of heat, the arsenic in the metallic form.

In this mode of detecting the presence of arsenic, it is necessary to avoid some sources of error, into which, without previous knowledge of their existence, an operator might easily fall. If the effervescence be rapid, it frequently happens that very minute portions of zinc, or of the salt of zinc generated, may be carried up by the stream of gas, and, being deposited upon the plate, form a crust, which might lead to suspicion, or perhaps wrong conclusions. This may be avoided by either moderating the effervescence, or by passing the gas, before using it, through a tube filled loosely with cotton, by which it is filtered, as it were, and all mechanically diffused particles separated. Much more important sources of error arise, however, from the existence of arsenic in most of the zinc and some of the sulphuric acid of commerce. The ores of zinc occasionally contain orpiment, which being reduced along with the other sulphuret, it is necessary to distil the zinc in order to have it pure, and to reject it as long as it contains arsenic. The iron pyrites also occasionally contains traces of orpiment, and this passes into the oil of vitriol. In employing this method, it is necessary, therefore, to test the purity of the zinc and sulphuric acid by the method itself. A jet of the hydrogen, evolved from the zinc and dilute sulphuric acid simply, should be burned, or the gas passed through a solution of ammonia-nitrate of silver for a quarter of an hour. If no trace of deposition of arsenic occur, the materials may be considered as pure, and the suspected liquor may then be employed with confidence in the result.

A more remarkable source of error arises from the fact that the compounds of antimony yield, under similar circumstances, a precisely similar gas, *antimoniuret of hydrogen*. It would anticipate too much the history of that metal to enter into the details of the means of distinguishing that gas from the arseniuretted hydrogen, but they will be fully described in their proper place.

Arsenious acid possesses the power of preventing the putrefaction of animal substances, and hence the bodies of persons that have been poisoned by it do not readily putrefy. The arsenious acid combines with the fatty and albuminous tissues to form solid compounds, which are not susceptible of alteration under ordinary circumstances. It hence has frequently occurred, that the bodies of persons poisoned by arsenic have been found, long after death, scarcely at all decomposed, and even where the general mass of the body had completely disappeared, the stomach and intestines had remained preserved by the arsenious acid which had combined with them, and by its detection the crimes committed many years before were brought to light and punished. In the cases where the whole body has been found fresh, it resulted from the person having survived for a length of time sufficient for the complete permeation of the tissues by the absorption of the poison; in the others, death had occurred while it was yet only in the intestinal tube. The absorption of the arsenious acid in cases where death has not been rapid, renders its detection possible in all the various organs, particularly where the poisoning has been produced, not by the administration

of a single dose, but by frequently repeated doses, each insufficient to produce rapid poisoning. The decision in such cases is rendered, however, extremely difficult by the fact, recently established, that the resemblance of function, so often alluded to, between arsenic and phosphorus, is such, that the latter element, which characterizes the animal tissues by its almost constant presence, may be replaced as a constituent of our organs by arsenic. Thus, the bones may contain arseniate of lime as a substitute for some of their proper phosphate of lime, and in the phosphoric salts, which are found in the blood, a similar replacement may occur. It is certain that the quantity of arsenic thus found naturally replacing phosphorus in the body is very small, but there is no necessary limit to its extent; and although, in cases of suspected chronic poisoning, the analysis of the organs might lead to useful evidence, yet the discovery of arsenic out of the alimentary canal should, as I conceive, not without great caution, be considered as necessarily involving its having been administered.

The sulphuret of arsenic of commerce, *king's yellow*, when taken as a poison, is recognised by its solubility in ammonia, from which it is again thrown down by an excess of any acid. Its reduction to the metallic state has been already fully described.

An antidote has been recently discovered to the poisonous effects of arsenious acid, which is founded on a very remarkable reaction When hydrated peroxide of iron is made into a thin paste with solution of arsenious acid, this disappears, being changed into arsenic acid, and the iron into protoxide, $2Fe_2O_3$ and $As.O_3$ producing $4Fe.O. + As.O_5$. This arseniate of iron has no action on the system; and hence, in cases of poisoning by arsenic, this hydrated peroxide should be administered as largely and as rapidly as possible. It may be made in a few moments by adding carbonate of soda to any salt of red oxide of iron (permuriate, muriate, or acetate tincture). It need not be washed, as the liquor contains only a salt of soda, which would be, if not beneficial, certainly not injurious.

The preparations of arsenic are of very extensive use in the arts. The metal is used to alloy the lead of which shot is made. White arsenic is employed in glass-making, to prevent the deoxidation of the oxide of lead, and the orpiment is employed to render indigo soluble in some processes of dyeing. It has many other less extensive uses.

Of Antimony.

This metal was first discovered, and its preparations introduced into medicine by Basil Valentine, from the unpleasant results of whose experiments upon his fellow monks it got the name of *antimoine;* its proper Latin name is *stibium*, and hence its symbol, Sb. Antimony exists in nature, principally as sulphuret, sometimes as oxide, and also these two combined, forming the oxysulphuret, red antimonial ore. It is from the native sulphuret that the metal is prepared. The process for obtaining it by means of iron is noticed p. 332, but it is had purer by fusing the sulphuret at a bright red heat with black flux. Sulphuret of potassium and oxide of antimony are first formed, and this last being decomposed by the car-

bon, carbonic oxide is evolved, and metallic antimony separates; this process is farther detailed in p. 334.

The antimony thus obtained is a brilliant white metal, of a highly crystalline fracture, and may be obtained crystallized in rhombohedrons, like those of arsenic, by fusion, as described in p. 23; its specific gravity is 6·8; it melts at about 800°, just below redness, and may be volatilized by a white heat. If heated violently in contact with air, it takes fire, burning with a brilliant white flame, and forming antimonious acid, which, though not volatile, is carried up by the current of air, and is deposited on the neighbouring bodies as a white powder, *flowers of antimony.* Antimony in powder takes fire spontaneously in chlorine, burning with a yellowish flame; the antimony is not oxidized by exposure to the air nor by water; it is not acted on by sulphuric nor muriatic acids, but is rapidly oxidized by nitric acid. The symbol of antimony is Sb.; its equivalent numbers are 1613 or 129·2; it combines with oxygen in three proportions.

Oxide of Antimony—$Sb.O_3$; equivalent 1913 or 153·2—may be prepared by adding to an acid and boiling solution of chloride of antimony in water, carbonate of soda in excess. The carbonic acid does not combine with oxide of antimony, which therefore precipitates pure; it is a white powder, not quite insoluble in water, and becomes yellowish when heated. If metallic antimony be burned in a limited supply of air, this oxide forms, and has been obtained crystallized both in the prismatic and octohedral forms of arsenious acid, with which it is, therefore, isodimorphous; both the metal and this oxide, when ignited in a full supply of air, produce antimonious acid.

This oxide of antimony combines with acids to form salts of very little stability, but it produces with the acid potash salts of the vegetable acids, double salts of remarkable constitution; of these the potash tartrate of antimony (*tartar emetic*) is the most important; it also acts as a feeble acid; thus, if in its preparation caustic potash be used to decompose the chloride, a granular white powder is obtained, in which the oxide of antimony is combined with potash; it is on this account called *hypo-antimonious acid* by many chemists.

Oxysulphuret of Antimony.—$Sb.O_3+2Sb.S_3$. This substance constitutes the red ore of antimony, and may be artificially produced by roasting the native sulphuret in contact with the air; the sulphur burns out as sulphurous acid, and the antimony becomes oxidized; the product generally contains an excess of oxide, which may be dissolved out by tartaric acid, and it is thus that the basis for tartar emetic is sometimes prepared; by continued roasting, the whole of the sulphur may be expelled, and an impure oxide of antimony produced; this, when melted, constitutes the glass of antimony, and the oxysulphuret is the crocus of antimony of the older pharmacopœias.

Antimonious Acid. Peroxide of Antimony.—$Sb.O_4$. Equivalent 2013 or 161·2. This is the most stable compound of oxygen and antimony; it is formed when antimony is oxidized freely, either by combustion or by the action of nitric acid, and igniting the resulting powder. It is a white powder, insoluble in water; it is not volatile;

it combines with alkalies, forming salts insoluble in water, and from which, by a stronger acid, it is separated as a hydrate, $Sb.O_4+H.O$. This hydrate dissolves in strong muriatic acid.

Antimonic Acid.—$Sb.O_5$. Equivalent 2113 or 169·2. This substance is first formed when metallic antimony is oxidized by an excess of nitric acid, and remains as a pale yellow powder, which, when exposed to a dull red heat, abandons one atom of oxygen, leaving antimonious acid, as just described; it is, however, more stable in combination, and may hence be prepared by deflagrating antimony with nitre; when the resulting mass is digested in cold water, nitrate and nitrite of potash dissolve out, and leave the *antimoniate of potash* as a white powder; this is decomposed by boiling water, which dissolves a basic salt, and leaves one with an excess of acid behind. In its hydrated condition, this acid dissolves in hydrochloric acid.

Antimony and sulphur combine in three proportions, forming sulphurets, which resemble completely, in constitution, the oxygen compounds; they are sulphur acids, dissolving in a solution of the alkaline sulphurets, and forming sulphur salts.

Sulphuret of Antimony.—$Sb.S_3$. Equivalent 2216·6 or 177·5. This substance constitutes the common gray ore of antimony, and crystallizes in the same form as orpiment, with which it is frequently contaminated; in its native state it is dark gray, with highly metallic lustre, crystalline in structure, and very easily reduced to powder; it may be prepared also by precipitation from a solution of any salt of oxide of antimony, as the chloride, or tartar emetic, by sulphuretted hydrogen; it is then an orange powder, which becomes darker on being dried, and has the same composition as the native sulphuret, with which it becomes identical in appearance by fusion. This sulphuret dissolves in alkaline solutions, on which circumstance are founded the various pharmacopœial processes for its formation. It has been used in medicine ever since the first discovery of antimony, and in all countries; the methods of preparation, and the purity of the products obtainable, are, therefore, exceedingly variable.

When finely powdered sulphuret of antimony is boiled in a strong solution of caustic potash, it dissolves, and the liquor contains two salts perfectly similar to one another, but containing, the one sulphur and the other oxygen, united to antimony and potassium. For one half of each substance is decomposed, the oxygen passing to the antimony, and the sulphur to the potassium, so that oxide of antimony and sulphuret of potassium result, and these respectively combine with the quantities of potash and sulphuret of antimony that had not been altered; in this way,

$$\left\{\begin{matrix} Sb.S_3 \quad 3K.O. \\ \text{and} \\ Sb.S_3 \quad 3K.O. \end{matrix}\right\} \text{produce} \left\{\begin{matrix} Sb.S_3+3K.S. \\ \text{and} \\ Sb.O_3+3K.O. \end{matrix}\right\}$$

When the solution cools, both compounds are partly decomposed, so that a quantity of sulphuret and of oxide of antimony precipitate mixed together; and hence an opinion has generally prevailed, and, indeed, been supported by the high authorities of Leibig and Gay Lussac, that these bodies are chemically united in the precipitate

so obtained, and that it is an oxysulphuret, identical in constitution with that already described. It is, however, quite established, particularly by the experiments of Berzelius and H. Rose, that the oxide and the sulphuret are but mechanically mixed; under the microscope, the former is seen as brilliant white crystals, mixed with the fine amorphous brown powder of the latter; and, besides, the quantity of oxide is completely variable, and in no case so great as the composition of the true oxysulphuret should require.

The precipitate thus obtained by cooling is generally of a fine orange brown colour, the exact shade of which varies very much with the temperature, and the degree of concentration of the liquor. It is termed in pharmacy *kermes mineral*, from a very remote analogy of its colour to that afforded by the insect *kermes* (*coccus ilicis*), which is used as a cheap substitute for cochineal.

After the separation of the kermes, the liquor, containing still the sulphur and oxygen salts above described, but with a greater proportion of base, is precipitated by adding an acid in excess. The sulphuret of potassium is decomposed, and the sulphuret of antimony, with which it had been combined, separates; at the same time, the sulphuretted hydrogen, evolved from the sulphuret of potassium, reacts on the oxide of antimony, converting it into sulphuret. This precipitate is much lighter-coloured generally than the kermes, and is sometimes called the *golden sulphuret of antimony*, although that name properly belongs to a different substance, to be described farther on. In many cases, in place of collecting the kermes and the portion precipitated by the acid separately as now described, the hot filtered liquor is added to the acid before the kermes has had time to separate, and the whole being then mixed, assumes an intermediate shade of colour, and constitutes the *brown sulphuret*, or *orange sulphuret of antimony* of the British pharmacopœias.

In place of caustic potash, the native sulphuret of antimony is frequently boiled with carbonate of soda. In this case the whole of the carbonic acid unites with one half of the soda, forming bicarbonate, and the other half of the soda acts with the sulphuret of antimony precisely as if it had been used in the caustic state.

An important mode of preparing these pharmaceutical substances consists in fusing the materials together instead of boiling their solutions. Thus an excellent kermes is prepared by fusing together three parts of native sulphuret and one of carbonate of potash. The general reaction is the same as described when the materials were dissolved; the melted mass is boiled in water, and the solution so obtained treated as already noticed. Rose has, however, directed attention to a circumstance which, though occurring in all cases, is more marked in this process than the others. It is, that some antimony separates in the metallic state, while another portion is changed into persulphuret; thus $5Sb.S_3$ produces $3Sb.S_5$, and $2Sb.$ is set free. The solution contains, therefore, not only the ordinary sulphuret, but some persulphuret of antimony, the colour of which is much brighter than that of the other, and it hence modifies the tint of the preparation in a variable manner. The persulphuret carries down with it also some sulphuret of potassium, and hence the

ordinary kermes mineral appears always to contain traces of potash. The quantity of persulphuret of antimony present seldom exceeds two or three per cent.

Sulpho-antimonious Acid.—$Sb.S_4$. This substance is produced as a yellow powder when the solution of antimonious acid is decomposed by sulphuretted hydrogen.

Sulpho-antimonic Acid--Persulphuret of Antimony, $Sb.S_5$—is obtained when a solution of antimonic acid in muriatic acid is treated with sulphuretted hydrogen. It is of a fine golden orange colour. Its formation in the process for kermes mineral has been already explained. This is the true *golden sulphuret.* To obtain it in large quantity, as is given in many pharmacopœias, three parts of sul phuret of antimony and one of carbonate of potash are to be fused with one half part of sulphur; this last converts the antimony into the persulphuret. The fused mass is to be dissolved in water, and decomposed by muriatic acid.

Antimoniuret of Hydrogen.—$Sb.H_3$. When hydrogen is evolved in contact with antimony in a nascent or finely divided state, they combine and form a gas, which, in properties and constitution, has a remarkable similarity to arseniuret of hydrogen. The easiest mode of effecting this is to dissolve zinc in dilute sulphuric acid to which tartar emetic has been added. The gas so evolved is colourless, insoluble in water, has neither acid nor alkaline reaction. It precipitates the salts of mercury and most metals, but not copper, by which it is distinguished from the arseniuret of hydrogen. Its specific gravity has not been experimentally determined; but if it be composed, like arseniuretted hydrogen, of one volume of metallic vapour and six of hydrogen condensed to four, it should be 4504·7. When this gas burns, water is formed, and antimony deposited, either as metal or as oxide, according to the supply of oxygen. It hence superficially resembles in its combustion the gas containing arsenic, but it is distinguished readily by the following characters.

1st. The antimoniuret of hydrogen, when it is decomposed by heating a point of the tube through which it passes to redness, deposites the metal at the heated part, while arsenic settles at a certain distance beyond, where the tube is colder.

2d. The metallic crust is not volatilized at any temperature which can be applied to glass.

3d. If the metallic scale be deposited on a porcelain plate, and oxidized by the outer flame of the blowpipe, it forms a powder yellow while hot, but white when cold, which is not volatilized by any farther application of the flame. Arsenic, on the contrary, becomes oxidized only in the act of being vaporized.

In certain cases of compound poisoning, and where tartar emetic has been given as an emetic in cases of poisoning by arsenic, it is possible that the two metals may coexist in solution. In these cases they may be separated by converting both into the hydrogen compounds, and decomposing the mixed gases by igniting the tube through which they pass. The antimony is deposited close to the heated part, and the arsenic at a little distance.

The detection of antimony is generally simple; in all its combinations it is immediately recognised by the formation of its com-

pound with hydrogen just described. In solution, in the state of oxide, it gives with sulphuretted hydrogen the orange precipitate of sulphuret. In the other states of oxidation the precipitates by sulphuret of hydrogen are more yellow, but are all easily distinguished from orpiment by not being volatile, and from the bisulphuret of tin by yielding the antimoniuret of hydrogen. From the sulphuret of cadmium they are known by their solubility in hydrosulphuret of ammonia.

Of Tellurium.

This is one of the rarest of the metals, and, although classified with them, from its lustre and power of conducting electricity and heat, in which it is, however, far inferior to the others, it ranks naturally with sulphur and selenium, to which last it assimilates completely in its properties. It exists in nature, native, and combined with a variety of metals, gold, silver, antimony, lead, &c., forming ores of very indefinite constitution. Its extraction, which is still farther complicated by the presence of sulphur and selenium, would require too detailed description, and is too seldom an object with chemists to require description here. Its properties and principal compounds alone deserve attention.

Pure tellurium is silver white and very brilliant. It crystallizes easily in rhombohedrons. It is brittle and easily powdered. Its sp. gr. is 6·14. It is about as fusible as antimony, and at a very high temperature may be volatilized. Its vapour smells like selenium; when heated in the air it burns with a bluish flame, forming tellurous acid. It is rapidly oxidized by nitric acid.

The analogy of tellurium to sulphur is very close. When tellurium is boiled in a strong solution of potash, there is formed tellurite of potash and telluret of potassium; but if this solution be diluted, the potassium reduces the tellurous acid, and the metal is precipitated, potash being regenerated. The symbol of tellurium is Te. Its equivalent numbers are 801·8 and 64·2.

Tellurium combines with oxygen in two proportions, forming tellurous and telluric acids. The former, *tellurous acid*, $Te.O_2$, is prepared by decomposing the bichloride of tellurium by water, $Te.Cl_2$ and $2H.O.$ producing $2H.Cl.$ and $Te.O_2$. This last precipitates as a bulky white powder containing combined water. In this state it is sensibly soluble in water, and reddens litmus. It dissolves readily both in acid and alkaline solutions, forming compounds of a very instable character. When its solution in water is heated to about 110°, it deposites the tellurous acid in an anhydrous form. The water is also expelled by a moderate heat from the hydrated acid in powder. The anhydrous acid thus obtained differs essentially from the hydrated form. It is insoluble in water, in acids, and in alkalies, and has no acid reaction whatsoever. No salts of it can be formed in the humid way; but if it be fused at a red heat with carbonate of potash, the carbonic acid is expelled, and tellurite of potash formed, which dissolves in water; from this solution the hydrated tellurous acid is thrown down on the addition of an acid.

Berzelius considers these remarkable differences of properties as indicating an isomeric distinction between the two acids. In a subsequent chapter I shall point out the manner in which I believe such compounds should be viewed.

Telluric Acid, $Te.O_3$, is prepared by deflagrating tellurous acid with nitre; a soluble tellurate of potash is thus obtained, which, when mixed with nitrate of barytes, gives an insoluble tellurate of barytes, and this, acted on by sulphuric acid, yields sulphate of barytes, and in solution telluric acid, which crystallizes in large prisms containing three atoms of water. Of these, two are given off at 212° F. It does not taste acid, but reddens litmus slightly. It combines readily with bases, forming classes of salts containing one, two, and four equivalents of acid. When the crystallized telluric acid is heated to redness, all its water passes off, it becomes orange, and undergoes a change of properties like stannic acid. It becomes insoluble in water, in acids, and alkaline solutions; when very strongly heated, it gives off oxygen, and tellurous acid remains; but if this anhydrous acid be fused with potash, the tellurate of potash which dissolves contains the acid in its hydrated state. These forms are considered as being isomeric, and not identical bodies; their real nature will be noticed hereafter.

Tellurium and hydrogen combine to form a gas, *telluret of hydrogen*, H.Te., which resembles in its characters sulphuret of hydrogen, particularly in its odour; it red-

dens litmus, is soluble in water, decomposes the alkalies and earths, forming soluble tellurets, and precipitates insoluble tellurets from solutions of the other metals.

Tellurium combines with sulphur in two proportions, forming sulphurets, which do not require detailed notice. Its compounds with the metals resemble so completely the metallic sulphurets as to render a separate account unnecessary. Thus, in every case where a metallic sulphuret evolves sulphuretted hydrogen gas with an acid, the telluret of the metal produces telluretted hydrogen, and the metallic tellurets are soluble or insoluble in water, precisely as the sulphurets of the same metals are.

Of Uranium.

This metal exists in some rather rare minerals, particularly in *pechblende*, combined with oxygen; the processes for its extraction are rendered very complex by the presence of a great number of other metals, and I shall refer, therefore, to the systematic works for the details of its extraction; the metal itself is easily obtained pure by the action of hydrogen gas on either of its oxides at a red heat. It is of a dark gray colour, difficultly fusible, specific gravity 9·0. Its symbol is U., its equivalents are 2711 or 217·3, being the largest numbers for any of the simple bodies; it combines with oxygen in two proportions.

Protoxide of Uranium, U.O., is obtained by decomposing any salt of uranium by a caustic alkali; it precipitates as a greenish hydrate, which rapidly becomes yellow, forming the peroxide by absorbing oxygen: the protoxide of uranium is dissolved by an excess of ammonia. *Peroxide of uranium*, $U.O_3$, is formed when the protoxide is heated in air; it is yellow, and possesses some of the characters of an acid, uranic acid; it reddens litmus; it enters into combination as well with alkalies as with acids; the alkaline and earthy uranates are insoluble, yellow or orange coloured. This oxide is used to colour glass of a fine lemon yellow.

The sulphurets, &c., of uranium are unimportant.

SECTION V.

METALS OF THE FIFTH CLASS.

Of Copper.

Copper is one of the most important of the metals, and one, also, of the most extensively diffused through nature. It exists native in veins, and frequently crystallized, in forms belonging to the regular system; in the state of oxide it is found, both uncombined and forming arseniates, phosphates, carbonates, and other salts, but its most abundant source is the native sulphuret. The ordinary copper ore, *copper pyrites*, is a double sulphuret of copper and iron, $Cu_2S.+Fe_2S_3$, and from this the metal is extracted for the purposes of commerce.

The general processes for the reduction of a metallic sulphuret have been already described (p. 333), but, from the composition of the copper ore, some additional management is required; there are two metals present in the ore, and as neither is volatile, the product after complete reduction should be, if the process was simply managed as for a simple sulphuret, not pure copper, but an alloy of one equivalent of copper and two of iron; this is avoided by arresting the process of reduction at a certain stage; the copper, having less affinity for oxygen than the iron, assumes the metallic state first, and, if it were possible to work so accurately, the whole of the copper might be reduced before any iron, and this last metal left altogether in the scoriæ as oxide or silicate; but this not being feasible, the copper first obtained is rendered impure by the presence of a quantity of iron, and also of sulphur; this impure copper is then calcined; the iron and sulphur, being the more combustible bodies, are first oxidized, and then again, by other reductions and calcinations, the copper is ultimately brought to a state of complete purity

The separation of the iron is facilitated by adding a small quantity of sand to the calcined mass before the process of reduction; the silicic acid unites exclusively with the oxide of iron, and the silicate of iron not being reducible under ordinary circumstances, the purification of the copper is more rapidly effected.

Though the copper is thus rendered quite pure from iron, great care is still required in these operations, in order to secure the proper softness, ductility, and tenacity necessary in the employment of this metal in the arts; thus, if it has been too long in contact with the fuel, it combines with a small quantity of carbon; if, on the other hand, the deoxidizing action of the fuel be not applied long enough, some suboxide remains undecomposed, which dissolves in the metallic copper. In both these cases the metal is brittle and of a bad grain, so as to be unfit for many of its uses.

Copper is obtained also in the metallic state by precipitation from the water which collects in the galleries and shafts of copper mines, and which, from the oxidation of the sulphuret of copper, contains sulphate of copper dissolved. Fragments of old iron are thrown into the reservoirs in which the drainage water of the mine is collected, and by electro-chemical action, as described p. 193, 195, and 335, the iron is dissolved and the copper precipitated in irregularly crystallized masses.

Pure copper is of a peculiar well-known reddish colour. It is very malleable and ductile; after iron, it is the strongest of the metals. It crystallizes by fusion in a form which is not the same as that found native, or produced when the metal is precipitated from its solutions. Its sp. gr. is 8·9. It is fusible at 1996°. It is not volatile. In dry air it is not tarnished, but in damp air it gradually becomes covered with a greenish coating of basic carbonate of copper. When heated in contact with air, copper combines rapidly with oxygen, and passes through a variety of rainbow colours, but is at last converted into black oxide, which forms as scales upon its surface. The series of colours arises first from the action of light upon the thin coating of oxide, as also happens in the oxidation of iron. The generality of acids do not act on copper at ordinary temperatures, unless in contact with air, for the copper is incapable of decomposing water; but at the point of contact with air, oxygen is directly absorbed, and the acid combines with the oxide so generated. In this way the feeblest acids may act upon copper, as the acetic acid and the acids contained in the various fatty bodies, and the metal be thus introduced into culinary preparations, and so produce poisonous effects. The acids which give off oxygen directly dissolve copper, as nitric acid, with evolution of nitric oxide. Strong oil of vitriol, also, when boiled on copper, gives sulphate of copper and sulphurous acid gas.

The symbol of copper is Cu., from its Latin name; its equivalent 395·7 or 31·7.

Copper combines with oxygen in two proportions, forming a suboxide and a protoxide.

Protoxide of Copper.—Cu.O. Equivalent 495·7 or 39·7. This oxide is formed by exposing copper, at a red heat, to a current of air. It may also be obtained by igniting the nitrate of copper. It is a

dull black powder, which, by a very high temperature, may be melted, and crystallizes on cooling. It dissolves but slowly in acids, forming the ordinary blue or green salts of copper. When heated, even below redness, in a stream of hydrogen gas, it is perfectly reduced, water being formed. It is thus that, as described in p. 253, the composition of water is best determined. At a dull red heat, this oxide is reduced completely by carbon and all its compounds, carbonic acid being produced. For this reason it is extensively employed in the ultimate analysis of organic substances, of which it converts the carbon into carbonic acid, and the hydrogen into water The metallic copper thus obtained by the reduction from the oxide is a fine pinkish-red powder, which has a remarkable affinity for oxygen, and is hence used in the analysis of organic substances containing nitrogen, to prevent the formation of nitrous or nitric oxides.

When a solution of caustic potash is added in excess to a solution of a salt of copper, the protoxide is thrown down as a hydrate, $Cu.O. . H.O.$ It is a fine blue powder, which is decomposed by a very gentle heat, so that even if a liquor containing it be boiled, it becomes brown and anhydrous, though in the midst of water. It is hence that, if the solution of copper be added to a boiling solution of potash, the precipitate is the dark brown anhydrous oxide, which, however, obstinately retains a little potash.

Suboxide of Copper.—Cu_2O. Equivalent 891·4 or 71·4. This body exists native, constituting the ruby copper ore, and may be prepared artificially by igniting a mixture of five parts of black oxide of copper and four of copper filings; half of the oxygen of the former passes to the latter, and the whole becomes suboxide. It is likewise made by fusing together three parts of subchloride of copper and two of dry carbonate of soda; chloride of sodium and suboxide of copper result, $Cu_2Cl.$ and $Na.O.$ giving $Cu_2O.$ and $Na.Cl.$, while the carbonic acid is given off. This suboxide of copper is a reddish-brown powder, which is much less acted on by moist air than pure copper; and hence, under ordinary circumstances, when copper becomes brown by being coated with this oxide, the action ceases. Articles of copper are thus coated intentionally, for the purpose of preserving their surface, by covering them with a paste of red oxide of iron, which, when heated, is thus reduced to the state of protoxide, $2Cu.$ and Fe_2O_3 giving $Cu_2O.$ and $2Fe.O.$; this last is then removed by digestion in a boiling solution of acetate of copper.

The generality of acids decompose the suboxide of copper into metallic copper, and the black oxide with which the acid combines; but, besides the subchloride of copper, several of its salts may be formed by the action of deoxidizing agents on the salts of the black oxide; thus sulphurous acid converts the hydrate of the black oxide into sulphate of the suboxide, $S.O_2$ and $2Cu.O.$ producing $S.O_3 + Cu_2O.$ From the solution of this salt, a fine orange hydrate of the red oxide is thrown down by the caustic alkalies. Protochloride of tin and protosulphate of iron also reduce the salts of copper to this state of oxidation.

Sulphur combines with copper in two proportions, forming sulphurets equivalent to the oxides just described; they are both found

native, and constitute, particularly the subsulphuret, important ores of copper. They may be prepared artificially by fusing together sulphur and metallic copper; the union takes place with brilliant combustion. If some sulphur be placed in a flask, and heat be applied so as to fill the flask with the vapour of sulphur, a thin copper wire dipped in it burns, as iron does in oxygen, forming the subsulphuret; these bodies are not of importance, except as the great sources of metallic copper.

The sulphurets of copper may also be formed by precipitating the salts of copper with sulphuretted hydrogen; a deep brown powder is produced, which is $Cu_2S.$ or $Cu.S.$, according as the solution contained the suboxide or the protoxide of the metal.

The detection of copper in solution is very simple; the salts of the black oxide are generally green or blue; on the addition of ammonia, a precipitate is produced, bluish or green, according to the acid with which the oxide had been combined, but in all cases producing with an excess of the ammonia a deep violet-coloured solution. The only metal which resembles copper in this respect is nickel, and from it, it is distinguished by all its other properties, particularly by the yellow prussiate of potash, which produces a fine chocolate brown precipitate of ferrocyanide of copper. With sulphuret of hydrogen, the salts of copper give a dark brown sulphuret, insoluble in hydrosulphuret of ammonia; and when a slip of clean iron or zinc is introduced into a liquor containing copper, this is reduced, and deposited upon the surface of the zinc or iron as a bright coating of metallic copper.

When the copper exists as suboxide, its reactions are very different; it gives, with ammonia, a white precipitate, which redissolves in an excess, forming a colourless liquor; if there be no excess of acid, chloride of sodium gives a white precipitate of subchloride of copper. But in practice it is never necessary to look for copper by these reactions, the salts of the suboxide absorbing oxygen with such avidity, that by a few minutes' exposure to the air their constitution changes. The colourless solution of suboxide of copper in ammonia becomes violet blue in the act of pouring it from one bottle to another; and hence, for the mere detection of copper, the properties of the protoxide alone need be taken into account.

Like the oxides of cobalt and nickel, the oxides of copper are not, by themselves, soluble in water of ammonia. The solutions of these metallic compounds in water of ammonia are basic salts, to the constitution of which the acid, with which the metallic oxide had been originally combined, is necessary. The detailed nature of these bodies will be noticed among the compounds of ammonia.

The detection of copper by the blowpipe is very simple and distinct. Fused with borax, a substance containing the most minute trace of copper gives a glass, which, when heated in the oxidizing flame, becomes green, being coloured by the protoxide; but when ignited in the reducing flame and suddenly cooled, is deep ruby red, generally opaque. This change of colour arises from the copper being reduced to the state of suboxide The colour given to glass by this suboxide is a pure prismatic red, so homogeneous that red light may be obtained for optical experiments by transmitting

white light through this coloured glass, and the tint is so fine that this ruby glass is the most valuable that can be used for ornamental purposes.

The salts of copper generally tinge the flame of the blowpipe blue or green, according to the other bodies that may be present.

Independent of the direct employment of copper in the arts, for which its properties eminently qualify it, it enters into the composition of a great number of alloys of great importance. Thus bronze, formerly used as a substitute for steel, and still employed in the casting of statues and monuments, from the accuracy with which it adapts itself to the mould, and its durability, consists of ninety parts of copper and ten of tin in 100. It is curious, that from the very earliest ages, this, which is still the best proportion, should have been employed; the bronze swords from ancient Egypt, from Scandinavia, and those found in Ireland, having all this constitution. *Gun metal*, or that of which cannons are cast, is an inferior kind of bronze, containing somewhat less tin.

The elasticity and sonorousness of these alloys are very remarkable. That used for bells, *bell metal*, consists of 80 parts of copper and 20 of tin. The Indian *gongs* have this composition, but common bells contain less tin, and, in place of it, some lead and zinc. In the proportion of two parts of copper to one of tin, or, more accurately, of four atoms of copper to one of tin, 127 to 59, an alloy is formed of exceeding brittleness and hardness, and so brilliant, when truly polished, as to be used for the mirror surface in reflecting telescopes; it is hence called *speculum metal*. The quality of this alloy is remarkably deteriorated by a slight deviation to either side of the true atomic proportions.

The alloys of zinc and copper are very numerous and important, constituting the different varieties of *brass*. The best brass consists of four atoms of copper to one of zinc; but, by changing the proportions of the metals, a variety of shades of gold lustre, used in counterfeit jewelry, are obtained. In the proportion of equal parts of copper and zinc, *hard solder* is produced; this is used in soldering together surfaces of brass and copper.

Of Lead.

This metal exists in nature, very extensively diffused, and in a great variety of forms. The sulphate, phosphate, arseniate, carbonate, and chloride of lead are found native; but it is exclusively from the sulphuret of lead, *galena*, that the metal is extracted for the purposes of commerce. The methods used in its reduction have been very fully described in the preceding chapter, p. 334.

Lead is one of the softest and least tenacious of the metals; it is bluish white, and very brilliant, but rapidly tarnishes in the air, becoming covered with a grayish coating, beyond which the action does not appear to extend; its specific gravity is 11·44; it melts at 612°, and in solidifying diminishes in volume, so that it is unfit for accurate castings; it may, however, be obtained, by fusion, crystallized in octohedrons; it is not volatile; it is not sensibly acted on by muriatic nor sulphuric acids, except at very high temperatures, but by nitric acid it is rapidly oxidized and dissolved.

When lead is exposed at the same time to air and moisture, its oxidation proceeds with great rapidity, so as to be used to analyze atmospheric air (p. 264). The oxide so formed is not quite insoluble, so that when pure water, rain, or even common soft water is preserved in leaden cisterns, an impregnation with lead may occur in such amount as to produce dangerous consequences, if employed habitually as a drink. Fortunately, this is obviated, in general, by the small quantities of saline matters, particularly sulphates, which all ordinary spring and river waters contain. These react on the oxide of lead, and, forming compounds totally insoluble in water, remove all traces of it from solution. A whitish crust gradually forms on the interior of the cistern, and assists, subsequently, in protecting it from the oxidizing action of the air; no danger is therefore to be apprehended from the supply of water to a city being conveyed through leaden pipes, and preserved in leaden cisterns; for all water of mineral origin dissolves, in filtering through the layers of rocks in its passage to the surface, a sufficiency of saline matters to serve for its protection.

The symbol of lead is Pb., from its Latin name; its equivalent is 1294·5 or 103·7. It combines with oxygen in two proportions, forming oxides, which, again uniting, form an intermediate complex oxide.

Protoxide of Lead.—Pb.O. Equivalent 1394·5 or 111·7. This may be prepared by exposing metallic lead at a red heat to a current of air; the lead rapidly combines with oxygen, and the oxide so produced fuses. It forms, on cooling, crystalline masses of a greenish-yellow colour; this constitutes the *litharge* of commerce, which is generally obtained in the cupellation of lead for the purpose of extracting from it the small quantity of silver which its ores generally contain. When the litharge is kept for some time, the masses of it break up into a brick-red crystalline powder, evolving heat. This change is technically termed *slacking*, but it is not due, like the slacking of lime, to combination with water, but to a change of the crystalline form of the litharge. The yellow form appears to be more permanent if the lead be oxidized at a lower temperature, and, when powdered, was once used as a yellow pigment under the name of *massicot.* This may be produced of the richest colour by decomposing the subnitrate of lead at a temperature insufficient for the fusion of the oxide.

This oxide may also be prepared by decomposing a soluble salt of lead by caustic potash; a white precipitate is produced, which is a hydrate of the oxide, 2Pb.+H.O.; by a great excess of caustic potash the precipitate may be redissolved. The oxide of lead appears to have the power of uniting with most of the alkalies and earths to form compounds more or less soluble. A body of this kind, formed by boiling lime and litharge together, is capable of crystallizing, and is used to dye the hair black. The hair contains sulphur, and a black sulphuret of lead forms in its substance, and is not liable to change. The protoxide of lead requires 12,000 parts of water to dissolve it; the solution reacts feebly alkaline; it is a strong base, and the only oxide of lead which combines with acids.

Peroxide of Lead, $Pb.O_2$, is obtained by digesting the protoxide

in chlorine water, or in a solution of chloride of lime. In the first case, 2Pb.O. and Cl. produce $Pb.O_2$ and Pb.Cl. In the second case, Pb.O. and Ca.O.Cl. produce $Pb.O_2$ and Ca.Cl.; another simple plan consists in heating red lead, which is a compound of the protoxide and the peroxide, with dilute nitric acid, until all the protoxide is dissolved out, washing the residue well, and drying it at a moderate heat. The peroxide so obtained is of a dull dark brown colour; when heated it gives off half its oxygen, leaving litharge. With muriatic acid it produces chlorine and protochloride of lead, and with sulphurous acid, which it rapidly absorbs, neutral white sulphate of lead, $Pb.O_2$ and $S.O_2$ producing $Pb.O.+S.O_3$. This oxide of lead does not form salts.

The *Red Lead*, or *Minium*, $Pb_3O_4=2Pb.O.+Pb.O_2$, is produced when lead is oxidized, so that the oxide formed shall not be fused, and when the metal is all converted into the yellow powder, increasing the heat to incipient redness. Oxygen continues to be absorbed until one third of the metal is converted into peroxide, giving the constitution above expressed. This is the pure red lead, the colour of which is exceedingly brilliant; but the generality of red lead found in commerce contains an excess of protoxide, which may be removed by boiling in a solution of neutral acetate of lead.

When red lead is ignited, it gives off oxygen and becomes protoxide; with muriatic acid it forms protochloride and chlorine. It does not form any proper salts, but it dissolves in acetic acid completely, giving a colourless liquor, from which, after a little time, peroxide of lead separates.

It is probable that there exist other oxides of lead; thus the gray coating which forms on lead exposed to the air is looked upon by many chemists as a suboxide; and on heating oxalate of lead to low redness, a gray powder is obtained of a similar nature, and yields, on analysis, the formula Pb_2O. In general, these bodies have been considered as mixtures of the metal in powder with the real protoxide; but I think the evidence of their definite constitution very strong.

From the similarity of the formula of red lead, Pb_3O_4, to those of the black oxide of iron, Fe_3O_4, and of the red oxide of manganese, Mn_3O_4, it has been suggested that it may contain sesquioxide of lead, Pb_2O_3, similar to Fe_2O_3 and Mn_2O_3. The formula of red lead should then become $Pb.O.+Pb_2O_3$; but this idea, though interesting, is only hypothetical.

Sulphuret of Lead.—There is but one compound of sulphur and lead, the protosulphuret, Pb.S. It constitutes the abundant lead ore, galena, and may be formed artificially, either by fusing together lead and sulphur, or by decomposing a solution of a salt of lead by sulphuretted hydrogen gas or hydrosulphuret of ammonia It is then a black powder, insoluble in water, and in alkalies, and dilute acids. It is rapidly oxidized by nitric acid, being converted into sulphate of lead. From the perfect insolubility and marked colour of this sulphuret, a salt of lead and sulphuretted hydrogen are respectively the most delicate reagents for each other.

There are some indications of the existence of other sulphurets of lead, which, however, do not require special notice. If a salt of

lead be decomposed by bisulphuret of calcium, a red precipitate appears, possibly a *bisulphuret of lead*, analogous to the deutoxide, and galena may be fused with metallic lead, forming a homogeneous mass, in which, probably, subsulphurets are contained.

The detection of lead is simplified very much by its forming but one series of salts, those of the protoxide. Its solutions are recognised by giving, with caustic potash, a white precipitate, soluble in excess; with carbonate of potash, one also white, but insoluble in excess; with sulphuretted hydrogen, one dark brown or black, whose characters are described above; with a solution of bichromate of potash, the salts of lead produce a fine yellow precipitate, *chrome yellow;* and with iodide of potassium, the iodide of lead, in brilliant yellow scales, like fragments of gold leaf. Yellow prussiate of potash gives a white precipitate, and sulphate of soda a white sulphate of lead, insoluble in water, but not insoluble in acids. If the solution contain much lead, any soluble chloride throws down sparingly soluble chloride of lead, which, however, remains dissolved, if the solution be dilute.

Lead and its preparations are of the most extensive use in the arts. In making pipes and cisterns, sulphuric acid chambers, bullets, and a variety of other purposes, the metal is employed unaltered; and its alloys are also of important application. Thus the metal of which printing types are made consists of three parts of lead to one of antimony. The inferior sorts of pewter are alloys of lead and tin, but the fine kinds should be tin with very little lead, and some antimony and bismuth. The solder used for soldering surfaces of lead, or of tinned iron, to each other, consists of lead and tin, the proportions of which vary from two parts of tin and one of lead, to three parts of lead and one of tin, according to the object. The more tin the alloy contains, the more fusible it is. *Fine solder* fuses at 360° *coarse solder* at 500°.

Of Bismuth.

Bismuth is not a common metal. It is found but in a few places, and only in the metallic state in quantity, for the sulphuret of bismuth is too rare to be of technical interest. It is extracted from the rocks through which it is disseminated by reducing them to coarse powder, and igniting this in a kind of kiln; the bismuth, being very fusible, melts out, and collects at the bottom in a trough placed to receive it.

It is a white metal, with a peculiar reddish shade, and remarkably crystalline structure. It may be obtained in separate crystals of considerable size, which are cubes, generally hollow at the sides. To obtain good crystals, the metal should be perfectly pure; this is effected by deflagrating some nitre on the surface of the melted metal; the impurities are more easily oxidized than the bismuth, and hence pass into the scoriæ which form on the surface. The crystals so obtained have frequently beautiful rainbow tints on their surface, from an exceedingly thin layer of oxide of bismuth by which they become coated.

Bismuth is very brittle and easily oxidized. It is scarcely acted on by sulphuric or muriatic acid, but it decomposes nitric acid vio-

lently, evolving nitric oxide, and forming oxide of bismuth, with which the nitric acid combines. It fuses at 497°, is volatile at a white heat, and then burns with a bluish-white flame. Its sp. gr. is 9·9.

The symbol of bismuth is Bi. Concerning its equivalent, there is some doubt at present as to whether it should be 886·9, or three times so much, 2660·7, on the oxygen scale, and hence 71·1, or 213·3, on the hydrogen scale.

The first number assumed would make the oxide of bismuth a protoxide, Bi.O., the last a teroxide, $Bi.O_3$. The ground upon which the former view stands is the supposed similarity of some salts of bismuth to those of magnesia and the protoxide of copper, but recent examination has gone to show that this analogy is not at all so strong as had been supposed, and that their difference is more remarkable than their resemblance. On the other hand, the sulphuret of bismuth is isomorphous with the sulphurets of antimony and arsenic, and the equivalent deduced from the specific heat of bismuth agrees with those for arsenic and antimony, and assigns the same constitution to the compounds of the three. The salts of the oxide of bismuth are exceedingly instable, and, like those of antimony, are decomposed by water, so that, while it allies itself to that metal in every important point of physical and chemical characters, it recedes in all the important facts of its history from copper, iron, zinc, and the other metals of the magnesian class. I therefore think these are sufficient grounds for abandoning the numbers 886·9 and 71·1, given in the table, p. 205, and to assume 2660·7 and 213·3, as the equivalents of bismuth on the oxygen and hydrogen scales respectively.

Oxide of Bismuth—$Bi.O_3$; equivalent 2960·7 or 237·3—may be prepared by the combustion of bismuth at a high temperature, or by the ignition of the subnitrate of bismuth. It is a buff-coloured powder, which may be melted. It combines with acids to form well-characterized salts.

The *Superoxide of Bismuth*, $Bi.O_5$, is prepared by boiling finely-levigated oxide of bismuth in a solution of chloride of soda. A fine brown powder is produced, which is freed with great difficulty from admixed unaltered oxide. When heated to dull redness it is decomposed into oxygen and oxide of bismuth; with muriatic acid it gives chlorine and ordinary chloride of bismuth. Its composition was supposed to corroborate the idea that the yellow oxide was a protoxide, for on that idea this would be a sesquioxide, Bi_2O_3, like the sesquioxides of cobalt and nickel, which it resembles so much in properties; but the formula, $Bi.O_5$, agrees as well with the analytical results, and I look upon it as corresponding to antimonic acid.

Sulphuret of Bismuth, $Bi.S_3$, exists native, in crystals isomorphous with the sulphurets of antimony and arsenic. It may be prepared by fusing bismuth and sulphur together, or by adding sulphuretted hydrogen to a solution of a salt of bismuth: it then precipitates as a brown powder. It is insoluble in water and in hydrosulphuret of ammonia.

Bismuth is easily known by its solutions being precipitated brown by sulphuretted hydrogen and by iodide of potassium, and yellow by chromate of potash. The caustic and carbonated alkalies produce a white precipitate of hydrated oxide of bismuth, which is insoluble in excess. A strong solution of a salt of bismuth is decomposed by the addition of water, whereby a white basic salt is precipitated, and the liquor contains free acid.

Bismuth is extensively employed for some purposes in the arts. The alloy used for casting stereotype plates consists of tin, lead, and bismuth; and by increasing the quantity of bismuth, the fusibil

ity of this alloy becomes so great, that a compound of two parts of bismuth, one of tin, and one of lead, fuses at 201°. This is the fusible metal used for the bath in taking the specific gravities of vapours, as described p. 14, and for supplying a steady source of heat for other purposes.

SECTION VI.

METALS OF THE SIXTH CLASS.

Of Silver.

This metal exists native, and in the state of sulphuret, in a great variety of places; and from the facility with which it may be extracted, and the permanence of its lustre, it became known at a very early period. The principal sources of silver are the mines of South America; in Europe, those of Saxony are the most remarkable. A great deal of silver is also obtained from the ores of lead, the sulphuret of lead being generally accompanied by the sulphuret of silver in small quantity.

The native silver of America exists, generally speaking, too finely disseminated to be simply melted out. It is washed out by mercury, this fluid metal dissolving the silver, and being then distilled off, leaves the precious metal behind. A very remarkable process is used to extract the silver from the sulphuret. This ore is roasted in a reverberatory furnace with chloride of sodium, by which chloride of silver and sulphuret of sodium are formed, Ag.S. and Na.Cl. giving Ag.Cl. and Na.S. This last is washed out, and then the chloride of silver being put into barrels with some water, pieces of iron, and mercury, the iron decomposes the chloride of silver, forming chloride of iron and setting the silver free, and this dissolves in the mercury, forming a fluid amalgam; this is strained through leather bags, by which a great part of the mercury passes off, and a pulpy mass of amalgam of silver is obtained, which is then submitted to distillation, by which the mercury is separated, and the silver remains pure.

The method of extraction of the silver which accompanies the lead, in galena, is founded on the greater rapidity with which lead combines with oxygen. In the smelting of the ore, the silver is reduced with the lead, and the resulting impure metal is melted in a shallow porous dish made of bone ashes, and when at a full red heat a current of air is urged across it from powerful bellows. The lead becomes converted into litharge, as described in p. 395, and new coatings of oxide of lead succeed one another upon the surface, until the whole quantity of that metal has been removed. When the silver remains pure, the surface becomes suddenly brilliant, and the completion of the work is known by the metal thus *flashing* or *lightening*, as it is technically termed. This is the process of *cupellation*. The porous bone earth capsule, or *cupel*, absorbs a great deal of the litharge, and the rest is blown away from the surface, as it forms, by the blast of air, and is collected in the front of the furnace.

This process has been remarkably shortened by the discovery

that the quantity of silver may be concentrated in a comparatively small quantity of lead, by crystallization. The silver is not diffused uniformly through all the lead, but combined in atomic proportions with a certain quantity of it, forming an alloy, which is then mixed with the excess of lead. This alloy is more fusible than lead, so that when a large basin of lead, containing a small quantity of silver, is melted, and allowed to cool very slowly, so as to crystallize, the portions which first solidify are pure lead, and these being removed with iron colanders, all the silver remains in the mother liquor. The process must be stopped, however, before this begins to congeal. By a succession of crystallization of this sort the great excess of lead is gradually got rid of, and the quantity to be oxidized at the cupel diminished in a corresponding degree.

The silver of commerce is never pure, and hence, for chemical purposes, must be freed from the metals, generally copper, associated with it. For this purpose it is dissolved in nitric acid, and its solution precipitated by common salt. Chloride of silver separates, which is then reduced by any of the methods described in p. 332, 333. The method of assaying may also be used to obtain pure silver. The impure silver is melted with from four to eight times its weight of lead, and this alloy cupelled as already detailed; the lead is not only itself oxidized, but the other metals present, which would not otherwise separate, are converted into oxides, which pass off with the oxide of lead. It is in this way that the standard alloys of silver, for coinage and plate, are verified at the mint and other offices.

Silver, when completely pure, is very brilliant; it is the whitest of the metals, and takes a fine polish. It is very ductile and malleable. Its sp. gr. is 10·5; it fuses at 1873°. It is not altered by air or water, but when kept melted for a considerable time, it absorbs oxygen, which it appears to hold rather dissolved than combined, for on solidifying it discharges this oxygen, by which the surface is thrown into irregular granulations. The quantity of oxygen may be so great as twenty times the volume of the metal.

Silver is very soft. It is hence necessary, in coin, and in articles for domestic use, to add a certain quantity of copper, to render it less liable to deterioration from use or in being cleaned.

When silver is exposed to the air, it gradually tarnishes, which is due, not to the formation of oxide, but of sulphuret, the air always containing traces of sulphuretted hydrogen, derived from organic bodies. It is not acted on by sulphuric or muriatic acid, but is rapidly dissolved by nitric acid, with evolution of nitric oxide gas.

Silver combines with oxygen in three proportions, forming oxides, of which only one, the protoxide, is well known. The equivalent of silver is 1351·6 or 108·3, and its symbol is Ag., from the Latin name.

Protoxide of Silver—Ag.O.; equivalent 1451·6 or 116·3—may be prepared by adding caustic potash, or lime water, to a solution of nitrate of silver. A brown powder is thrown down, which may be dried at a gentle heat without alteration. It then becomes very dark. When heated strongly, it is decomposed into oxygen and metallic silver, and this takes place even at ordinary temperatures,

if it be in contact with organic matter. It neutralizes the strongest acids, as the sulphuric and nitric, and forms well-characterized salts. It is not acted on by the fixed alkalies, but with ammonia it gives *fulminating silver*, one of a series of bodies to be hereafter examined. When citrate of silver is heated to 212° in a current of hydrogen gas, the metal is not reduced, as should have occurred with the pure oxide, but one half of the oxygen is removed, and the citric acid remains combined with the *suboxide of silver*, Ag_2O. This salt dissolves in water, the solution being brown, and giving a brown precipitate of suboxide with potash. When a solution of this salt is heated, it becomes colourless, contains a salt of the peroxide, and metallic silver separates. Some other silver salts of organic acids give the same result with hydrogen gas. When a solution of nitrate of silver is decomposed by the battery, a substance is deposited upon the positive electrode in needles, sometimes half an inch long. These are resolved by sulphuric acid into protoxide of silver and oxygen, and give, with muriatic acid, chloride of silver and free chlorine. They are, therefore, crystals of *peroxide of silver*, probably $Ag.O_2$.

Although silver does not combine with oxygen directly, yet when it is heated in contact with glass, it stains this of a deep yellow or orange colour, being converted into oxide.

Sulphuret of Silver, equivalent 1552·8 or 124·4, exists native pure, and also in combination with other metallic sulphurets, particularly those of lead, antimony, copper, and arsenic, forming a variety of minerals. It is the most common ore of silver. It may be formed artificially by fusing together sulphur and silver, the excess of sulphur being expelled by the heat. Silver has, indeed, a remarkable affinity for sulphur, so that it even decomposes sulphuretted hydrogen, and hence arises the tarnishing of silver when exposed to the atmosphere. An exceedingly delicate test for sulphur in a solid body consists in igniting a minute fragment of it on charcoal, in the reducing flame of the blowpipe; the fused globule is to be then laid on a bright surface of silver, as on a clean shilling, and moistened; if there be a trace of sulphur in the substance, a black or olive spot will form on the silver where it is moistened.

The sulphuret of silver may be formed also in the wet way, by adding sulphuretted hydrogen or hydrosulphuret of ammonia to a solution of a salt of silver. It forms as a black powder, which is not soluble in an excess of the precipitant. This sulphuret is a powerful sulphur base, and in its native forms is generally associated with negative metallic sulphurets.

The detection of silver is very easy; from the facility with which its oxide is reduced to the metallic state, its solutions are precipitated by the sulphites, by protosulphate of iron, and by protochloride of tin, the silver being reduced. A solution of common salt or muriatic acid gives a white curdy precipitate of chloride of silver, which is insoluble in water and in acids, but dissolves in water of ammonia; when exposed to light in contact with organic matter, the chloride of silver becomes tinged violet or black, owing to the formation of a subchloride; on this is founded its application in photography, described p. 173. The solutions of silver give, with

iodide of potassium, a canary-yellow precipitate, insoluble in ammonia, and with sulphuretted hydrogen a deep brown sulphuret of silver.

The uses of silver are well known ; its advantages as a medium of exchange depend on the steadiness of the quantity of it brought into commerce, which prevents great changes in its value, and on its not being corroded or worn down by ordinary agents. In a pure state it would, however, be too soft to be used as coin, and is hence hardened by being alloyed, in the proportions of 222 parts to 18 of copper; this is the standard silver of the mint; the silver used for the purposes of luxury contain a greater, but a variable quantity of copper.

Of Mercury, or Quicksilver.

From the remarkable properties of this metal, and its occurring in the metallic state in nature, it has attracted much attention from the earliest ages, and formed the object of the most elaborate inquiries of the older chemists. Its volatility and the variety of its compounds made it enter into the theories of that period as an important element, and hence there is, perhaps, no metal concerning which so much valuable knowledge was obtained in the infancy of chemistry.

Mercury is found native, and also combined with gold and silver, but its most abundant ore is the native sulphuret, *cinnabar;* from this it is extracted by one or other of two processes. The first consists in distilling the ore with lime, or with iron in small pieces; in the first case, Hg.S. and Ca.O. produce Ca.S., while Hg. and O. pass off, the temperature being too high to allow of the formation of oxide of mercury; in the second case, Hg.S. and Fe. produce Fe.S. and Hg.; this process is carried on in long furnaces, in which are arranged numbers of earthen or iron retorts, to which are adapted receivers, in which the mercurial vapours condense. The other plan, which is that now adopted in the best arranged works, consists of a kiln, like that in which the pyrites is roasted for the manufacture of oil of vitriol: below, there is a grate on which is lighted a fire of brushwood; over this is a light arch of fire-brick, with numerous perforations, and on this is arranged the cinnabar, the poorest kinds being placed below, until the kiln is filled nearly to the orifice of the chimney, which passes off at the side; the fire communicating to the ore, the sulphur contained in it burns, and the mercury is set free, Hg.S. and 2O. producing $S.O_2$ and Hg. The kiln is so hot that the metal is completely volatilized, and the mixed vapour of mercury and sulphurous acid gas are carried by the draught into the chimney, which leads into a wide chamber of brick-work, the sides of which are hung with leather; on these the mercury condenses in drops, which gradually flow down and collect on the floor, while the sulphurous acid gas passes away by a small chimney at the farther end, by means of which the continuous combustion of the ore is sustained; at certain periods, an aperture in the side of this chamber is opened, and the mercury which had collected is withdrawn.

The mercury is sent into commerce in iron bottles, but generally

in a very impure state, it being intentionally adulterated with the alloy of tin, lead, and bismuth, already noticed p. 398, of which it can dissolve large quantities. It may be purified by distillation, or by being left for some time in contact with dilute nitric acid. The mercury, having less affinity for oxygen than any of the other metals present, is the last to dissolve, and as soon as the liquor is found to contain mercury, the metal remaining may be looked upon as pure.

Mercury is distinguished by being liquid at ordinary temperatures; this, together with its resemblance to silver in brilliancy, is the origin of its various names, *hydrargyrum* (*υδωρ αργυρεος*), *quicksilver*, *argentum vivum*. If pure, it is not tarnished by exposure to the air, but in damp air its impurities become oxidized very rapidly, in consequence of a complete galvanic circuit being formed with the mercury and the other metals present. At 39° it becomes solid, and crystallizes in octohedrons; it then contracts very much; its sp. gr. being 13·5 when liquid, and 14·0 when solid. At 662° it boils, and forms a colourless vapour, the sp. gr. of which is 6978. At and just below its boiling point it absorbs oxygen from the air, forming oxide, which at a red heat is again decomposed.

Mercury is not acted on at common temperatures by sulphuric or muriatic acid; nitric acid oxidizes it rapidly, the nature of the product varying with the circumstances. Boiling oil of vitriol is decomposed by mercury, sulphurous acid being evolved, and oxide of mercury produced. There are two oxides of mercury, a suboxide and a protoxide. The symbol of mercury is Hg., from its Latin name, and its equivalent is 1265·8 or 101·4.

Suboxide of Mercury.—Hg_2O. Equivalent 2631·6 or 210·8. This oxide is the basis of many important preparations, and is best prepared by decomposing calomel (subchloride of mercury) by a solution of potash. The calomel being insoluble, the action must be favoured by mixing the two together well by agitation in a mortar; a black powder is produced, which must be dried in the dark, and by a very gentle heat. In this process, $Hg_2Cl.$ and K.O. produce K.Cl. and Hg_2O. Lime water may be used in place of potash. When this suboxide, or, as it is often called, black oxide of mercury, is heated, it is resolved into metallic mercury and the protoxide, and this change occurs slowly at ordinary temperatures if it be exposed to the light. This oxide combines with acids and forms well characterized salts.

Protoxide of Mercury—Hg.O.; equivalent 1365·8 or 109·4—may be prepared in a variety of ways: 1st. By exposing mercury for a long time to the action of the air, at a temperature just below its boiling point, it is gradually converted into small deep red crystals of this oxide; in this state it was the *red precipitate per se* of the older chemists. 2d. By heating crystals of nitrate of mercury until all the water and nitric acid have been expelled, the oxide remaining is a crystalline powder of an orange-red colour, the *red precipitate by nitric acid.* 3d. When a solution of chloride of mercury (corrosive sublimate) is decomposed by caustic potash or lime water, Hg.Cl. and K.O. produce K.Cl. and Hg.O. It is thus obtained as a canary-yellow hydrate, which, however, when dried, becomes deeper coloured. The red precipitate also, when finely divided, assumes the same yellow tint.

This oxide of mercury is slightly soluble in water. The solution browns turmeric paper slightly, and restores the blue colour of reddened litmus. It combines with acids, forming a numerous and important class of salts. At a full red heat it is totally resolved into mercury and oxygen, as described fully in page 242. It changes its colour remarkably with the temperature, becoming nearly black when very hot.

Subsulphuret of Mercury, Hg_2S., may be prepared by decomposing any salt of the suboxide by hydrosulphuret of ammonia. It is a black powder, which, on the application of heat, is decomposed into the protosulphuret and metallic mercury.

Protosulphuret of Mercury—$Hg.S.$; equivalent 1467 or 117·5—constitutes the native cinnabar, the usual ore of quicksilver. It may be prepared artificially by fusing sulphur in a crucible, and adding thereto six times its weight of mercury; they combine with the evolution of considerable heat. The mass must be stirred frequently to favour their union, and covered in order to prevent the sulphur from burning away. In this state it is black, but when sublimed at a red heat in glass vessels, it becomes deep red, constituting *factitious cinnabar*, and this, when levigated, and exposed to strong light, in flat dishes covered with a thin layer of water, gradually assumes a very brilliant colour, and forms the pigment *vermilion*. This sulphuret may also be prepared by adding to a solution of corrosive sublimate an excess of hydrosulphuret of ammonia or sulphuret of hydrogen; it is then a dense black powder. It may, however, be obtained red, but not so bright as vermilion, in the wet way, by digesting white precipitate (chloramide of mercury) with hydrosulphuret of ammonia, to which an excess of sulphur has been added. The sulphuret of mercury forms at first black, but after some time becomes red, which colour may be brightened by the action of a warm solution of caustic potash.

The phosphurets and seleniurets of mercury are of no importance.

The presence of mercury in solution is very easily ascertained. By the immersion of a clean slip of copper, the mercury is precipitated in the metallic state, as a gray powder on the surface of the copper. With a magnifying-glass, this is found to consist of minute but brilliant globules, and the surface becomes brilliant when rubbed. Protochloride of tin and phosphorous acid also precipitate the mercury in the metallic state, which, by boiling, aggregates into larger globules, easily collected and recognised. Any solid body containing mercury gives, when ignited in a tube of hard glass, particularly on the addition of a little carbonate of potash, a sublimate of metallic mercury, which, if in very small quantity, appears only as a ring of gray powder, but is found to consist of brilliant globules when inspected with a lens.

The two classes of salts which quicksilver forms are very distinctly characterized by their behaviour to reagents. The salts of the suboxide give with the caustic alkalies black or gray precipitates. Sulphuretted hydrogen produces the black subsulphuret. Solution of chloride of sodium gives a white precipitate, which is calomel, and the bichromate of potash produces an orange chromate of the suboxide.

The salts of the red oxide are precipitated, yellowish by an excess of caustic potash, and white by ammonia; with sulphuretted hydrogen in excess, a black precipitate of protosulphuret; and with iodide of potassium, a red precipitate, which is redissolved in an excess.

In many cases, the appearance of these precipitates varies with the nature of the acid with which the oxide of mercury had been combined; but in all cases ammonia gives a black precipitate with the salts of the suboxide, and a white precipitate with those of the red oxide, in the cold.

There is a class of pharmaceutical preparations obtained by triturating mercury with other inactive substances. In these the mercury is only reduced to a state of very minute division; it is not oxidized. By triturating mercury with sulphur, however, a certain quantity of sulphuret is formed, although the great mass of the metal and of the sulphur remains uncombined.

Of Gold.

This valuable metal is found only in the metallic state, either pure or alloyed with other metals, particularly silver, tellurium, and mercury; the rocks in which it is found distributed are generally those of igneous origin, but the greater part of the gold of commerce is obtained by washing the sands of the rivers which have their source in such mountains, the particles of metal being carried down with the detritus of the rock, and, from their greater density, being deposited first when the sand is washed; any fragments large enough to be visible are separated by the hand, but the remainder is dissolved out by a process of amalgamation, similar to that described, p. 399, for the extraction of native silver. When the gold is alloyed with silver, they are separated by means of nitric acid, which dissolves the latter metal; but if the quantity present be small, the gold protects it from the action of the acid, and a process termed *quartation* is employed; this consists in alloying the gold with three times its weight of silver, and then acting on the mass with nitric acid; when the solution of the silver has once commenced, it does not cease until the entire quantity present has been removed.

Pure gold is yellow, very malleable and ductile, and nearly as soft as lead; hence, for the purposes of commerce and of the coinage, it is alloyed with a quantity of copper, amounting to 83 in 1000. Instances of the exceeding degree of division to which this metal may be reduced, have been given, p. 15. Gold has no tendency to combine with oxygen or sulphur, and hence retains its brilliancy in the open air for any length of time. It melts at 2016°; its density is 19·5; it is not acted on by any single acid, but is dissolved by nitromuriatic acid, and by a mixture of nitric and hydrofluoric acids.

The symbol of gold is Au., from its Latin name, and its equivalent numbers are 2486 or 199·2.

There are two oxides of gold, obtained by the decomposition of the corresponding chlorides, which will be hereafter described. The deutoxide of gold, $Au.O_2$, is a green powder, which does not combine with acids, but dissolves in solution of caustic potash, and soon separates into the higher oxide and metallic gold. The *perox ide of gold, auric acid*, $Au.O_3$, is best prepared by decomposing per

chloride of gold by an excess of magnesia; chloride of magnesium dissolves, and an insoluble aurate of magnesia remains; this is to be then digested in cold dilute nitric acid, which dissolves out the magnesia with a little auric acid, but leaves the greater part of this last behind as a reddish hydrate, which, when dried in the air, becomes brown, and at 212° gives off water, and remains black. This substance does not combine with any acid; by muriatic acid it is decomposed, perchloride of gold being formed; it combines with alkalies strongly, so that the precipitate given by a solution of gold with a caustic alkali is always a compound of auric acid with the base; there are soluble and insoluble aurates, but their atomic constitution has not been studied. Solutions of auric acid, and even that body in powder, are decomposed rapidly on exposure to the light, metallic gold being separated.

Gold is deposited from its solutions by means of any of the deoxidizing agents noticed under silver and mercury. Protosulphate of iron gives a brown powder, which, under the burnisher, assumes the colour and brilliancy of the metal; protochloride of tin produces a fine purple precipitate, the *purple of Cassius*, which is not metallic gold, but it appears to be a compound of oxide of tin and a suboxide of gold, for it is perfectly soluble in water of ammonia, and mercury digested on it does not dissolve out any metallic gold. Various processes are given for this preparation, which it is not easy to obtain of the proper depth and purity of colour; when exposed to a red heat, it is changed into a mixture of peroxide of tin and metallic gold, but its purple colour remains; it is hence employed for painting on glass and porcelain. When metallic gold is heated on the surface of glass, it appears to become oxidized, and in that state to combine with the glass, staining it a rich purple colour.

Sulphur and gold combine to form sulphurets similar in constitution to the oxides; they are produced by decomposing the corresponding chlorides by sulphuretted hydrogen; they are brown powders, which are strong sulphur acids, and dissolve in hydrosulphuret of ammonia.

The uses of gold are well known. The commercial value of its alloys is ascertained, either by cupellation, p. 399, by quartation, p. 405, or by the touchstone, which is a variety of flinty slate (Lydian stone) or basalt, of a uniform black colour. A streak is drawn on the surface of the stone with the piece of gold to be tried, and this is compared with those given by a series of alloys, the composition of which is known, until one is found identical in aspect with it, which must result from the two being of the same degree of purity. In these trials it is necessary, however, to know beforehand whether the alloy is silver or copper, or whether, as frequently occurs, both be present.

Of Palladium.

This metal is found associated with platinum, but seldom constitutes more than one per cent. of the ore. After the platinum has been precipitated from the solution in aqua regia, by means of sal ammoniac, cyanide of mercury is added, by which all the palladium

is thrown down as cyanide; this, when ignited, is totally decomposed, and metallic palladium remains.

The general characters of palladium are very similar to those of platinum; it is white, almost infusible, but admits of being welded; it is malleable and ductile; specific gravity 11·5. When heated below ignition, its surface becomes blue and green, from the formation of a thin layer of suboxide; but by a stronger heat this is reduced, and the metal becomes bright. Palladium is not sensibly acted on by muriatic or sulphuric acid, but it dissolves in nitric acid with facility. The symbol of palladium is Pd., and its atomic weight 665·9 or 53·4.

There are three oxides of palladium, of which only one, the protoxide—Pd.O.; equivalent 765·9 or 61·4—has been as yet studied with much care; this oxide is formed when palladium dissolves in nitric acid, and is obtained as a black powder when the nitrate is decomposed at a temperature below redness; by the addition of potash to a salt of palladium, this oxide is thrown down, hydrated, as a brown powder. If the protoxide of palladium be exposed to a dull red heat, it parts with half its oxygen, and a *suboxide*, Pd_2O., is produced, which gives a series of salts, resembling in general characters those of the suboxide of copper.

By decomposing the bichloride of palladium with carbonate of potash, the *deutoxide*, $Pd.O_2$, is obtained as a yellowish brown powder; it appears to combine both with acids and alkalies, but of its properties very little is known.

There are *sulphurets of Palladium*, which correspond to the oxides, but farther than that they are brown powders, generated by the action of sulphuret of hydrogen on the respective chlorides, they have not been much examined.

Palladium in solution is at once recognised by giving with ammonia a flesh-red precipitate, which redissolves in an excess, giving a colourless solution; with cyanide of mercury it produces a whitish precipitate, and with iodide of potassium, a black powder.

Of Platinum.

Platinum was originally discovered in the sands of some South American rivers, and from its similarity to silver (*plata*), obtained the name of platina (little silver). It has since been found more abundantly in the mountains of the Oural, which separate European from Asiatic Russia. The supply of platinum has increased so much lately, that a coinage of it, issued some years ago by the Russian government, was obliged to be recalled, from the rapid diminution in value which it underwent.

The platinum exists native, but is associated with a great number of metals, particularly four, remarkable for not being found except along with it. The grains of metal are disseminated in rocks of igneous origin (granite, syenite), and in the sands of rivers which flow over them. The processes for the extraction of platinum from the crude ore are very complex, and as the working of it has become a branch of manufacture, the chemist always obtains the pure metal in commerce, and its details need not be inserted.

Pure platinum is white like silver, but not so brilliant. It is the densest of all bodies, its sp. gr. being 21·5. It is very malleable and ductile. It is infusible except by the hydro-oxygen blowpipe, but at a high temperature may be welded like iron, and thus worked into the various forms in which it is employed in the chemical arts. Platinum may also exist in a state of minute division, and thereby becomes useful in many operations, particularly those of slow combustion, as noticed in p. 180, 250, 287. The finely-divided platinum is of two kinds, *spongy platinum* and *platinum-black*. The former is

prepared by dissolving chloride of platinum and sal ammoniac sep arately in alcohol, and mixing the solutions; the double chloride of platinum and ammonium is thus produced as a fine yellow powder, which, while yet moist, is to be made into balls like peas, and heated to full redness. The chlorine is all carried off by the hydrogen of the ammonia, and the platinum remains as a light gray sponge, in the form of the little balls; it is this kind of platinum that is used in the aphlogistic lamp, in the eudiometer, and for other purposes already noticed. The *platinum-black* may be obtained either by precipitating a solution of bichloride of platinum with zinc, and boiling the precipitate in muriatic acid for a few minutes; or, better, by dissolving protochloride of platinum in a boiling solution of potash, and adding thereto alcohol, in small quantities at a time, until all effervescence ceases; a jet-black precipitate is produced, which is to be boiled successively with alcohol, muriatic acid, and potash, and, finally, four or five times in water. The substance thus obtained is pure metallic platinum, but it is a dull black powder. It absorbs oxygen in considerable quantity, and hence, when brought into an atmosphere of any inflammable vapour, it facilitates the combination of the two with remarkable energy. Dœbereiner terms it an *oxyphorus* from this property. Many interesting reactions in organic chemistry succeed only by the aid of this platinum-black.

Platinum has no tendency to combine with the oxygen of the air, but it is oxidized slightly when nitre or even potash is fused in contact with it. It resists the action of all acids except the nitro-muriatic acid and the nitro-hydrofluoric acids, and in these it dissolves more slowly than gold.

The symbol of platinum is Pl. Its equivalent is 1233·5 or 98·8. By the decomposition of the chlorides of platinum, two oxides of it are obtained.

Protoxide of Platinum—Pt.O.; equivalent 1333·5 or 106·8—is produced by digesting the protochloride with as much potash as exactly suffices for its decomposition. An excess of potash dissolves it, forming a dark olive liquor. When pure it is a black powder, easily decomposed by heat into platinum and oxygen. It combines with acids, forming salts, which have been as yet but little studied.

Deutoxide of Platinum.—$Pt.O_2$. Equivalent 1433·5 or 114·8. This substance has a remarkable tendency to combine with bases, and hence cannot be obtained pure by the direct decomposition of the chloride, as it carries down with it, always, a quantity of the alkali employed, if this be in excess; and if it be not, then only a basic chloride is obtained. The nitrate of platinum, however, when decomposed by soda, yields one half of the oxide of platinum, pure, but hydrated, forming a brown powder like the peroxide of iron; when anhydrous, it is black; by heat it is resolved into oxygen and platinum. This oxide appears to form two kinds of salts, one with acids, in which it is the base, and the other with alkalies and earths, in which it is the acid. In another place I shall notice them farther.

There are two *sulphurets of Platinum* corresponding to the two oxides. The first, Pt.S., is produced by digesting the protochloride with sulphuret of hydrogen. It is a deep brown powder, decomposed by a red heat, but not otherwise interesting. The bisulphuret, $Pt.S_2$, is produced in a similar way by adding sulphuret of hydrogen to a solution of bichloride of platinum. It is a brown powder, which absorbs oxygen rapidly even in drying, and becomes acid. By nitric acid it is converted with intense action into sulphate of platinum.

Phosphurets and seleniurets of platinum have been formed, but they are not important.

The detection of platinum is effected easily by precipitating its solution by a slip of zinc, when a black powder separates, soluble

only in aqua regia, and then giving with reagents the following results. A solution of sal ammoniac in alcohol gives a fine yellow crystalline precipitate; a solution of iodide of potassium a black precipitate, which dissolves in an excess, producing a rich crimson solution; with sulphuret of hydrogen, the brown bisulphuret of platinum; and with protochloride of tin, a chocolate precipitate or a deep reddish solution, according to the quantity present.

The action of this last reagent is founded on the reduction of the bichloride of platinum to the state of protochloride by the first portion of protochloride of tin employed. This test acts, therefore, also with solutions of the protoxide of platinum, and the metal may be also known to be in the state of protoxide, when, on the application of iodide of potassium in excess, the liquor is not coloured red, but becomes so on the addition of a drop of nitric acid or chlorine water.

The great use of platinum is for the manufacture of the large boilers used in the concentration of oil of vitriol; it is also universally employed as the material for the crucibles used in the more delicate operations of mineral analysis. Indeed, the accuracy now attained in that department of research is in a great part due to the introduction of platinum vessels into the laboratory; it is also accasionally used in enamelling on glass and porcelain.

Of Iridium and Rhodium.

These metals are, like palladium and iridium, found only associated with platinum, and are extracted from the crude ore already noticed; the iridium and osmium are, however, united, forming an alloy, the crystalline grains of which are merely mixed with the particles of the platinum ore in which the rhodium and palladium are contained; when the platina ore is dissolved in aqua regia, the iridium and osmium ore remains undissolved, and requires to be treated by fusion with caustic potash; the iridium then becomes oxidized, and combines with the alkali. The processes of purification need not be inserted.

Metallic iridium resembles platinum, but is still more infusible; when fused by the voltaic battery, it is white and very brilliant; specific gravity 18·68; after being strongly heated, it is insoluble in acids, but when obtained in the spongy form by the reduction of its oxides by hydrogen at a red heat, it becomess lightly oxidized, and is soluble in aqua regia.

Iridium combines with oxygen in four proportions; its symbol is Ir., and its equivalent 1233·5 or 98·8, the same as that of platinum.

Protoxide of Iridium, Ir.O., is obtained by decomposing the protochloride by carbonate of potash; it appears as a greenish-gray hydrate; this oxide combines with acids. The *sesquioxide*, Ir_2O_3, is that formed when the metal is ignited with potash; it is a bluish-black powder, and is the most permanent of the oxides; it is not decomposed except at a heat above the melting point of silver, whereas the higher and lower degrees pass into it on the application of heat. This oxide unites with acids, giving dark blood-red coloured salts. The *deutoxide of Iridium*, $Ir.O_2$, exists combined with acids, but has not been isolated. The *peroxide*, $Ir.O_3$, is formed in small quantity when iridium is ignited with nitre, but is best prepared by the decomposition of the perchloride. Solutions containing salts of the protoxide and of the peroxide together, present a great variety of shades of purple and blue, and hence gave origin to the name of the metal (Iris).

Rhodium.—This metal remains dissolved in the nitromuriatic solution of the platinum ore after the platinum and palladium have been separated from it; for the mode of eliminating it from the many metals which still remain, I refer to the systematic works.

Metallic rhodium is obtained by the decomposition of its chloride at a red heat by hydrogen gas; when rendered coherent by pressure, it is white, but very brittle and hard; sp. gr. about 11·0. If completely pure, it is not acted on even by aqua regia, but it illustrates remarkably the principle of communicated affinity, described p.

237; for, when alloyed with copper, lead, or platina, it dissolves along with the other metal in aqua regia. Rhodium derives its name from the beautiful rose (ροδος) colour of its solutions; it combines with oxygen in two proportions; its symbol is R., and its equivalent 661·4 or 52.2.

Of the *protoxide of Rhodium*, it is only known that it exists in certain salts that have been but little examined; the *sesquioxide*, R_2O_3, is the basis of the most important compounds of this metal. It is prepared by igniting metallic rhodium with a mixture of caustic potash and nitre; a brown mass is formed, which, when decomposed by muriatic acid, yields the oxide as a gray hydrate, insoluble in acids. Berzelius is of opinion that there are two isomeric forms of this oxide, the salts of one being yellow in solution, and those of the other being rose-coloured. There are supposed to exist, also, complex oxides of rhodium, resembling, probably, the complex oxides of iron and manganese. The equivalent of rhodium is so nearly equal to that of palladium, that some relations might be expected in the constitution of their combinations, which, as yet, does not appear to have been experimentally investigated.

CHAPTER XIV.

ON THE GENERAL PROPERTIES AND CONSTITUTION OF SALTS.

The bodies included under the name of salts may be arranged in two classes, characterized by a remarkable difference of chemical constitution; the first comprehends such as are formed by the union of a simple body of the chlorine family with a metal; thus chloride of sodium, iodide of potassium, bromide of iron, fluoride of calcium, are of this kind. The salts of the second class, on the contrary, are formed by the union of substances already compound, and possessed of those opposite properties by which one is determined to be an acid and the other a base. The general characters of acids and bases, and of the salts formed by their union, have been sufficiently described in many places already (p. 151, 154, 157), and need not be here repeated. In general, the acids and bases so engaged contain oxygen as their electro-negative ingredient; but there are classes of salts formed by the union of sulphur acids and sulphur bases, and, as noticed in p. 238 and 294, selenium and tellurium resemble oxygen and sulphur in this respect. The history of the metallic compounds in the last chapter affords many cases of the existence of such salts, and in the detailed history of the more important salts which will follow, others will be described; but there are some points of more general interest, touching the salts as a class, the laws of formation to which they are subjected, and the relations between their several subdivisions, which I shall now proceed to notice as briefly as the subject will admit.

I have frequently adverted to the circumstance that the bodies termed *hydracids* were in reality not acids, but compounds of hydrogen, in which that element acted as a positive metallic constituent; and that, when they act on a metallic oxide, double decomposition generally occurs, precisely as when a chloride or iodide of zinc or copper is decomposed by potash or by soda. Thus Cl.H. and K.O. produce Cl.K. and H.O., precisely as when Cl.Cu. and K.O.

produce Cl.K. and Cu.O. The chlorides and iodides of hydrogen, although popularly called acids (muriatic and hydriodic acids), are thus really salts, and in all their reactions display that constitution. Also, when a hydracid is put in contact with a metal, the solution of it is determined altogether by its power of expelling the hydrogen and of taking its place. From Cl.H. and Zn. there are produced Cl.Zn., and H. becomes free, precisely as chloride of copper, Cu.Cl., is decomposed by zinc, copper being precipitated. The hydracids, therefore, do not unite with metallic oxides to form salts, but they decompose them, water being evolved.

The hydracids are capable of forming what are termed acid-salts; thus the fluoride of potassium combines with hydrofluoric acid to form an acid compound; the chloride of hydrogen combines with chloride of gold: but these bodies are really double salts. The compounds of hydrogen, in such combinations, resembling the corresponding compounds of zinc, copper, &c., which, under the same circumstances, all form corresponding double salts.

I have already described the functions of water in the hydrates of the ordinary oxygen acids: these are salts of water, subject to the same rules of composition as the ordinary salts of the same acid. When such an acid, as, for example, oil of vitriol, $S.O_3+H.O.$, acts upon a metallic oxide, the water is displaced, and a salt of the metallic oxide formed. When such a hydrated acid acts on a metal, this may be dissolved either by substitution for, and displacement of the hydrogen, as in the ordinary cases of obtaining that gas, or by the direct decomposition of a part of the acid, as in the processes for obtaining sulphurous acid and nitric oxide (p. 285, 274).

Salts may be either *neutral*, *acid*, or *basic*. A salt is neutral which does not manifest, in its action on vegetable colours, acid or alkaline properties, and consists generally of one equivalent of acid united to one equivalent of base, this last containing one equivalent of oxygen. The true neutral salts have, therefore, for bases, either suboxides or protoxides. The salts of sesquioxides and deutoxides generally react like acids, except where there is an excess of base. The quantity of acid with which metallic oxides are disposed to unite in their most neutral salts, is subject to a remarkable proportion, being one equivalent for each atom of oxygen which the base contains. Thus a protoxide or suboxide combines with one equivalent of acid. The sulphate of zinc is $Zn.O..S.O_3$; sulphate of copper $Cu.O..S.O_3$; the subnitrate of mercury, $Hg_2O..N.O_5$. A sesquioxide unites with three equivalents of acid, as sulphate of alumina, $Al_2O_3+3S.O_3$. Salts in which this law is observed to hold are generally described as neutral, even though their action on vegetable colours may indicate a preponderance of acid; and understanding by the word, not the absence or presence of the property of changing turmeric or litmus, but the state in which the characteristic properties of acid and base are most neutralized, the definition of a neutral salt may best be that in which the number of atoms of acid is equal to the number of atoms of oxygen in the base

There are two kinds of *acid salts:* 1st, those in which the excess of acid is present in its hydrated form; and, 2d, those in which the dry acid is in excess. These differ remarkably in nature, those

of the first class being not really acid salts, but double salts, of which one base is water. Thus the common bisulphate of potash, of which the formula is $K.O..S.O_3+H.O..S.O_3$, is one of a family of double salts, in which sulphate of potash is united to a sulphate of a protoxide, as sulphate of copper, of zinc, of iron, or of magnesia. There is thus really no excess of acid. In like manner, the bicarbonate of potash is a double carbonate of potash and water, $K.O..C.O_2+H.O..C.O_2$, to which similar analogies exist. These salts resemble completely the acid salts of the hydracids, described in the beginning of this chapter; $K.O..S.O_3+H.O..S.O_3$ corresponding exactly to $K.F.+H.F.$

It is only the salts which do not contain water that can be looked upon as having a true excess of acid. Of these, the chromates of potash afford the best examples, in which an atom of potash is combined with one, two, or three equivalents of acid, forming $K.O.+Cr.O_3$, $K.O.+2Cr.O_3$, and $K.O.+3Cr.O_3$. There exists a similar compound of sulphuric acid and potash, which is easily decomposed by water, being changed into the ordinary bisulphate.

Basic salts are those in which there is present more than one equivalent of base for each equivalent of acid; thus, in turbeth mineral there is $3Hg.O.+S.O_3$; in basic nitrate of copper, $3Cu.O.+N.O_5.H.O.$; in basic sulphate of copper, $4Cu.O.+S.O_3+4H.O.$ It has been thought that the proportion of base in basic salts bore a simple relation to the quantity of oxygen in the acid, being generally equal to it. This idea was founded on the circumstance that the early analyses of many basic sulphates gave the proportion of three atoms of base to one of acid; but the basic sulphate of mercury is the only example I have found really to exist of that constitution, the other sulphates containing always a quantity of metallic oxide, amounting to two, or four, or six equivalents.

The first and most remarkable insight into the constitution of basic salts which we obtained was the principle laid down by Graham, that all salts are really neutral in constitution. The analogies of hydrogen to the magnesian family of metals, and hence of water to the oxides of that class, suggested the idea that the excess of base should not be considered as actually combined with the acid, but that it replaced the water of crystallization which the neutral salt contains. This view was remarkably supported by the evidence of the basic nitrates adduced by Graham, and has been extended to the chlorides and sulphates by my own investigations. Thus nitrate of copper, in its crystallized and neutral condition, is $Cu.O..N.O_5+3H.O.$, and the basic nitrate is formed by $H.O..N.O_5+3Cu.O.$ Comparing these two with the hydrated nitric acid, sp. gr. 1·42, the formulæ

Nitrate of water,	$=H.O..N.O_5+3H.O.$
Nitrate of copper,	$=Cu.O..N.O_5+3H.O.$
Basic nitrate of copper,	$=H.O..N.O_5+3Cu.O.$

evidently correspond, the only difference being that, in place of oxide of hydrogen, there is oxide of copper substituted, in a proportion continually increasing. From these conditions it follows, that with the same acid and base there may be formed a great va-

riety of basic salts; for the neutral salt may crystallize with many different proportions of water, and from each there may be one or more basic salts derived, by substitution of metallic oxide. Thus the sulphate of zinc generally contains eight atoms of base to one of acid; and in its common crystallized form, these consist of one of oxide of zinc and seven of water; but in becoming basic, the quantity of oxide of zinc gradually increases, and a series of basic salts is formed, as

$$S.O_3+Zn.O.+7H.O., \qquad S.O_3+6Zn.O.+2H.O.,$$
$$S.O_3+4Zn.O.+4H.O., \qquad S.O_3+8Zn.O.$$

The salts, consisting of a simple body of the chlorine family united with a metal, as chloride of sodium, iodide of potassium, &c., and which, from the analogy of common salt, are termed *haloïd salts* (ἁλς and ειδος), combine frequently with the oxide of the metal which they contain, and form *basic haloïd salts*. Thus we have Cu. Cl.+3Cu.O., basic chloride of copper; Hg.Cl.+3Hg.O., basic chloride of mercury; Pb.I.+2Pb.O., basic iodide of lead. Such compounds are, however, generally termed *oxychlorides*, *oxyiodides*, &c.; they are subjected to precisely the same laws of derivation and constitution as the basic salts of the same metals with ordinary acids.

From what has been said above, it might be concluded that a neutral salt consisted in all cases of one equivalent of base united to one of acid, and that, wherever the base was present in larger quantity, the salt should necessarily be termed *basic;* but an important distinction requires to be here laid down. There are three phosphates of silver, which contain respectively one, two, and three atoms of oxide of silver united to one atom of acid; but we do not consider the first as being neutral, and the others as containing an excess of base, for we find them to arise from the state of the phosphoric acid, which, according as it has been combined with more or less basic water, gives origin to classes of salts containing one, two, or three equivalents of oxide. The peculiar relations of the phosphoric acid, and of arsenic acid also, to water, and the effect of it on the composition of these salts, have been noticed already in p. 297 and 377. In addition, therefore, to ordinary neutral salts, which are *monobasic*, or contain an equivalent of base and one of acid, there are *bibasic* and *tribasic* salts, containing respectively two and three equivalents of base to one of acid, and yet being neutral; by which is meant, not that they are without action on test paper, since one tribasic salt may redden litmus, while another may brown turmeric paper, but that they are derived from a definite combination of the acid with basic water, and not by the replacement of the water of crystallization by metallic oxide, as in the case of real basic salts.

A simple distinction between *bibasic* and *tribasic* salts on the one hand, and ordinary basic salts on the other, is, that in the former the different atoms of base may be of different kinds, while in the latter the metallic oxide replacing the water is all of the same sort. Thus, there is basic sulphate of zinc and basic sulphate of copper, but there could not be a basic sulphate partly of zinc and partly of copper, the sulphuric acid being *monobasic*. But there is a tribasic

phosphate of soda, ammonia, and water; another of magnesia, ammonia, and water; others of potash and water. The presence of two or more bases of different kinds thus distinguishing completely the salts of the bibasic and tribasic acids from the ordinary basic salts.

These principles, which are now of the highest importance in philosophical chemistry, were first applied by Graham to the salts of the phosphoric and arsenic acids, but they have been found to throw light upon some of the most difficult questions in the history of the organic acids, of which a great number have been shown by Liebig to be similarly circumstanced.

Double salts are formed by the union of two simple salts. In general, both salts contain the same acid, but different bases, and the two bases belong to different natural groups; as when sulphate of potash combines with the sulphates of the protoxides of the metals of the second isomorphous group, replacing therein the atom of constitutional water which they all contain. Thus ordinary sulphate of zinc, $Zn.O. . S.O_3 . H.O.+6Aq.$, gives with $K.O. . S.O_3$ the double salt $(Zn.O. . S.O_3+K.O. . S.O_3)+6Aq.$; and sulphate of copper, $Cu.O. . S.O_3 . H.O.+4Aq.$, gives $(Cu.O. . S.O_3+K.O. . S.O_3)+4Aq.$ The sulphate of potash combines also with the sesquioxides of the third isomorphous group, such as alumina, and gives origin to the various kinds of alums. Similar classes of salts are formed by the union of the other alkaline sulphates with the sulphates of the second and third isomorphous groups. The salts of isomorphous bases with the same acid do not appear capable of combining so as to produce double salts, but in crystallizing are mechanically mixed (p. 31). This rule, however, is not without exception, as the constant composition of the magnesian limestone, $Ca.O. . C.O_2+Mg.O. . C.O_2$, indicates that its elements are chemically united.

Salts of different acids with the same base may combine to form double salts, as the oxalate and nitrate of lead; and there are examples, though few, of a double salt containing two acids and two bases.

The relations of salts to water have been fully discussed under the heads of solution and crystallization (p. 22, *et seq.*), and of the chemical properties of water (p. 253), to which it is sufficient to refer.

The haloid salts combine together to form double salts, as the double chloride of gold and sodium, the double chloride of copper and potassium, and conform therein to the same general principles that have been just described for the oxygen salts.

It has been always mentioned, that when muriatic acid acts on a metallic oxide, water is formed, and a chloride of the metal produced. The question of whether this always occurs is not without interest, and has been often agitated. There is no doubt but that it is the general rule, but I am inclined to think it may not be without exception. The difference of properties of the chlorides of magnesium and of aluminum in the anhydrous state and when crystallized with water, is so great as to give reason to suppose that these chlorides decompose water, and that the crystallized hydrated salts are not $Al_2Cl_3+3H.O.$ and $Mg.Cl.+H.O.$, but $Al_2O_3+3H.Cl.$ and

$Mg.O.+H.Cl.$ Hence it is probable that magnesia and alumina combine with hydracids without decomposition.

The *sulphur salts* consist of a sulphur acid, which is generally a sulphuret of an electro-negative metal or of carbon, combined with a sulphur base, which is a sulphuret of an electro-positive metal. In their constitution they resemble the analogous oxygen salts. Many of their characters have been described already (p. 282, 386).

The positive metallic sulphurets combine frequently with the haloid, or oxygen salts of the same metal, to form basic salts; this is the case particularly with mercury. Thus there is $Hg.O. \,.\, S.O_3+2Hg.S.$, similar to $Hg.O. \,.\, S.O_3+2Hg.O.$, ordinary turbeth mineral.

It had been long remarked as curious, that bodies so totally different in composition as the compound of chlorine with a metal on the one hand, and of an oxygen acid with the oxide of the metal on the other, should be so similar in properties, that both must be classed together as *salts*, and should give origin to series of basic and acid compounds for the most part completely parallel. This difficulty has been so much felt by the most enlightened chemists, that doubts have been raised as to whether the acid and base, which are placed in contact to form by their union an oxygen salt, really exist in it when formed; and it has been suggested that at the moment of union a new arrangement of elements takes place, by which the structure of the resulting salt is assimilated to that of a compound of chlorine or of iodine with a metal. This view, at first sight so far fetched, which considers that in Glauber's salt there is neither sulphuric acid nor soda, but sulphur, oxygen, and sodium, in some other and simpler mode of combination, is now very extensively received by chemists; and I shall proceed, therefore, to describe, with some detail, the form which it has assumed, and the evidence by which it is supported.

The greater number of those bodies which are termed oxygen acids have not been in reality insulated, and what are popularly so called are merely supposed to contain the dry acid combined with water. Thus the nearest approach we can make to nitric acid is the liquid $N.O_6H.$; to acetic acid, the crystalline body $C_4H_4O_4$; and to oxalic acid, the sublimed crystals $C_2O_4H.$; we look upon these bodies as being combinations of the *dry acid* with water, and we write their formulæ $N.O_5+H.O.$, and $C_4H_3O_3+H.O.$, and $C_2O_3+H.O.$; but that these dry acids exist at all is a mere assumption. Hence, with regard to these instances, and they embrace the majority of all known acids, the idea that the acid and base really exist in the salt formed by the action of hydrated acids on a base is purely theoretical.

When we compare the constitution of a neutral salt with that of the hydrated acid by which it is formed, we find the positive result to be the substitution of a metal for the hydrogen of the latter; thus $S.O_3+H.O.$ gives with zinc $S.O_3+Zn.O.$; and where a metal is acted on by a hydrated acid, the hydrogen is thus evolved either directly as gas, or it reacts on the elements of the acid, and gives rise to secondary products which are evolved, such as sulphurous acid, nitric oxide, &c. In all cases we may consider the action of a metal on a hydrated acid to be primarily the elimination of hy-

drogen and the formation of a neutral salt. But in this respect the action becomes completely analogous to that of the metal on a hydracid, except that in the latter case a haloid salt is formed; and hence we assimilate the two classes in constitution by a very simple arrangement of their formulæ.

There are, however, a number of acids which may be obtained in a dry and isolated form, as the sulphuric, the silicic, the telluric, the stannic, the arsenic, the phosphoric, &c.; and when they combine with bases, it is most natural to consider the union as being direct, and that the salt contains acid and base really as such. This is, accordingly, the strongest point of the ordinary theory. But other and important circumstances intervene. These acids, although they may be obtained free from water, yet in that state they combine with bases but very feebly, and require a high temperature in order to bring their affinities into play. On the other hand, in all cases where these bodies manifest their acid characters in the highest degree, they are combined with water, as in oil of vitriol and phosphoric acid, and when expelled from combination with a base, they immediately enter into combination with water in an equivalent proportion. Thus, where phosphate of lime is decomposed by oil of vitriol, it is not phosphoric acid ($P.O_5$) which is found in the liquor, but its terhydrate ($P.O_5+3H.O.$), as is shown by its forming with oxide of silver the yellow phosphate, $P.O_5+3Ag.O.$ In the case of telluric acid, its hydrate ($Te.O_3+3H.O$) is very soluble in water; it crystallizes in large prisms; by 212° two atoms of water are given off, but its nature is not changed; the body which remains ($Te.O_3+H.O.$) is still acid and soluble in water, perfectly neutralizing the alkalies; but by a red heat this last atom of water is driven off, and then the whole nature of the body changes; it is insoluble in water, and even in the strongest alkaline solutions, and can only be brought back to its former state by being fused with potash at a red heat. Here it is evident that the acid properties and the water go together; and we may conclude that, in order to manifest strong acid properties, the acid must be in its hydrated form. But in that hydrated form, if the water acted as a base simply, the tendency of the acid to combine with other bases would be inferior to that of the dry acid; for if we place oil of vitriol and barytes together, the water must be first expelled before the barytes and sulphuric acid can unite, and hence an impediment would exist to their union which would not occur with cold barytes and dry sulphuric acid in vapour, and yet cold barytes and oil of vitriol will combine with such intensity as to produce ignition, while the barytes must be heated before it begins to combine with the dry sulphuric acid. The water, therefore, is essential to the manifestation of strong acid properties, and it does not exist in combination with the acid merely as a base. What, then, is the constitution of a hydrated oxygen acid?

When muriatic acid ($H.Cl.$) acts on zinc, the metal is taken up, forming $Zn.Cl.$, and hydrogen is expelled; and if, in place of zinc, oxide of zinc be taken, the effect is the same, except that the hydrogen combining with the oxygen of the oxide forms water, $H.Cl.$ and $Zn.O.$ giving $Zn.Cl.$ and $H.O.$ Now we have in oil of vitriol

the elements $S.O_4H.$ combined together; when put in contact with zinc, H. is expelled, and $S.O_4Zn.$ is formed; and with Zn.O. and $S.O_4H.$, there are produced $S.O_4Zn.$, and H.O. is set free. In both cases, of which the former may be taken as the type of all the haloid salts, and the latter of all salts formed by oxygen acids, there is H. as the element, which is removable by a metal, precisely as one metal is replaceable by another, as, indeed, from the real metallic character of hydrogen, may be considered to occur in this case. Every acid may therefore be considered to consist of hydrogen combined with an electro-negative element; which may be *simple*, as chlorine, iodine, fluorine; or may be compound, as cyanogen, $N.C_2$, and yet capable of being isolated; or, as occurs in the great majority of cases, its elements may be such as can only remain together when in combination. Thus oil of vitriol does not contain $S.O_3$ and H.O., but consists of hydrogen united to a compound radical $S.O_4$. Liquid nitric acid does not contain $N.O_5$ and H.O., but consists of hydrogen united to a compound radical $N.O_6$, and the acetic acid is written $C_4H_3O_4+H.$, the oxalic acid $C_2O_4+H.$, and so on.

The elegance and simplicity with which the laws of saline com bination may be deduced from these principles is really remarkable Thus it has been remarked as a fact substantiated by experiment, that in neutral salts the number of equivalents of acid was propor tional to the number of equivalents of oxygen in the base, but the ordinary theory gave no indication of why this should occur. It follows necessarily from the principles of the newer theory. Thus, if a protoxide be acted on by an acid, M. denoting the metal of the oxide, and R. the radical of the acid, the resulting action is,

$$M.+O. \text{ and } H.+R. \text{ produce } H.+O. \text{ and } M.+R.;$$

and in the neutral salt, there is an equivalent of each. Now in the case of a sesquioxide, in order that water shall be formed, and so neither acid nor base in excess, the reaction is that

$$M_2+O_3 \text{ and } 3(H.+R.) \text{ produce } 3(H.+O.) \text{ and } M_2+R_3,$$

a sesqui-compound being formed perfectly analogous to a sesqui oxide, and the number of atoms of acid, 3(H.+R.), is equal to the number of atoms of oxygen in the base (M_2O_3), because that number of atoms of hydrogen is required for the decomposition of the base. In like manner, for a deutoxide, there is

$$M.+O_2 \text{ and } 2(H.+R.) \text{ producing } 2(H.O.) \text{ and } M.+R_2.$$

The power of salts to replace water in the magnesian sulphates, so as to form double salts, becomes much more intelligible when we compare H.+O. with $K.+S.O_4$, than where H.O. was contrasted with the complex formula $K.O.+S.O_3$.

The circumstance that on the new theory (or, as it is now often called, the *Binary theory of salts*) it is necessary to admit the existence of a great number of bodies (these *salt-radicals*) which have never been isolated, and in favour of whose existence there is no other proof than their utility in supporting this view, becomes more powerful as an objection when we proceed to apply its principles

to the salts of phosphoric acid. For it has been already described that this acid forms three distinct classes of salts, all neutral, and which have their origin in the three hydrated states of the phosphoric acid. These states are written on the two views as follows:

	Old Theory.	New Theory.
Monobasic acid,	$P.O_5+H.O.$ . . .	$P.O_6+H.$
Bibasic acid,	$P.O_5+2H.O.$ . . .	$P.O_7+H_2.$
Tribasic acid,	$P.O_5+3H.O.$ . . .	$P.O_8+H_3.$

Now it appears very useless, where the older view accounts so simply for the properties and constitution of these salts, to adopt so violent an idea as that there are three distinct compounds of phosphorus and oxygen, which no chemist has ever been able to detect. But here, again, other circumstances must be studied; first, the difference of properties of phosphoric acid, in its three states, is totally inexplicable, on the idea of their being merely three degrees of hydration. Nitric acid forms three hydrates, but when neutralized by potash, it always gives the same saltpetre; sulphuric acid forms two perfectly definite hydrates, but with soda forms always the same Glauber's salt; while phosphoric acid, when neutralized by soda, gives a different kind of salt according to the state it may be in. Also, the permanence of these conditions of phosphoric acid is a powerful proof that they do not consist in the adhesion of mere water. The idea that the phosphoric acid is a different hydracid in each of its three conditions, on the other hand, not merely explains the fact of these differences of properties, but it renders the formation of bibasic and tribasic salts, which is such an anomaly on the old theory, a necessary consequence of the new; for the phosphoric salt radicals, $P.O_6$, $P.O_7$, and $P.O_8$, differ not merely in the quantity of oxygen they contain, but are combined with different quantities of hydrogen, and hence, in acting on metallic oxides (bases), there is a different number of atoms required for each to replace the hydrogen and form water. Thus,

$P.O_6H.$ and $Na.O.$ give $H.O.$ and $P.O_6Na.$, monobasic phosphate of soda;
$P.O_7H_2$ and $2Na.O.$ give $2H.O.$ and $P.O_7Na_2$, bibasic phosphate;
$P.O_8H_3$ and $3Na.O.$ give $3H.O.$ and $P.O_8Na_3$, tribasic phosphate.

A circumstance which gives additional reason to infer that the water is not merely as base in the phosphoric acid, is the following: if it were so, then it should be most completely expelled by the strongest bases, and the bibasic and tribasic phosphates of the alkalies should be those least likely to retain any portion of the basic water; but the reverse is the fact; while oxide of silver, a very weak base, is that which most easily and totally replaces the water. On the idea, however, of hydracids, this is easily understood, for the oxide of silver is one most easily reduced by hydrogen, and, consequently, one on which the action of a hydrogen acid, as $P.O_8+H_3$, or $P.O_7+H_2$, would be most completely exercised.

A remarkable verification of this theory has been recently found in the decomposition of solutions of the oxysalts in water by voltaic electricity. It has been already explained (p. 187, *et seq.*) that it re-

quires the same quantity of electricity to decompose an equivalent of any binary compound, such as iodide of lead, chloride of silver, muriatic acid, or water. Now, if we dissolve sulphate of soda in water, and pass a current of voltaic electricity through that solution, we have water decomposed, and also the Glauber's salt; oxygen and sulphuric acid being evolved at one pole, and soda and hydrogen at the other. Here, on the old view, the electricity performs two decomposing actions at the same time, and, as it thus divides itself, its action on each must be lessened, and the quantity of each decomposed be diminished, so that the sum should represent the proper energy of the current. On measuring these quantities, however, the result is totally different; the quantity of sulphate of soda decomposed is found to be equal to the full duty of the current, and an equivalent of water appears to be decomposed in addition. It is quite unphilosophic to imagine that the strength of a current should be thus suddenly doubled, and a simple and sufficient explanation of it is found in the new theory of salts. The sulphate of soda in solution having the formula $Na.S.O_4$, is resolved by the current into its elements Na. and $S.O_4$, as chloride of sodium would also be; the sodium, on emerging at the negative electrode from the influence of the current, instantly decomposes water, and soda and hydrogen, of each an equivalent, are evolved; at the positive electrode, the compound radical $S.O_4$ also decomposes water, and produces $H.S.O_4$ and O. The appearance of the oxygen and hydrogen is thus but secondary, and the body really decomposed by the current is only $Na.S.O_4$.

In the case of the salts of such metals as do not decompose water, the phenomena are much more simple. Thus, a solution of sulphate of copper, when decomposed by the battery, yields metallic copper at the negative, and sulphuric acid and oxygen at the positive electrode, and the quantity of copper separated represents exactly the energy of the current which has passed; for the salt being $Cu.S.O_4$, is simply resolved into its elements, but $S.O_4$ reacting on the water, produces $H.S.O_4$, and O. at the positive electrode. On the old view it was supposed that water and sulphate of copper were both decomposed, oxygen and acid being evolved at one side, and oxide of copper and hydrogen being separated at the other; which reacting, produced water and the metal. Such an explanation, however, is directly opposed to the law of the definite action of electricity, and cannot be received.

In the case of solutions of chlorides or iodides, where there can be no doubt of the relations of the elements, the results of voltaic decomposition are precisely similar. Chloride of copper gives simply chlorine and copper, no water being decomposed. Chloride of sodium or iodide of potassium give chlorine or iodine at the one electrode, and alkali and hydrogen at the other; the evolution of these last being caused by the action of the metallic basis on the water of the solution.

Professor Daniell, to whom these important electro-chemical researches are due, considers the truth of the binary theory of salts to be fully established by them.

If this theory be adopted, a profound change in our nomenclature of salts will become necessary. Graham has proposed that the

name of the salt-radical should be formed by prefixing to the word *oxygen*, the first word of the ordinary name of the class of salts, and that the salts be termed by changing *oxygen* into *oxides*. Thus S. O_4, *sulphatoxygen*, gives sulphatoxides; the sulphates, N.O_6, nitratoxygen, gives nitratoxides, the nitrates, and so on; but I consider that the form of nomenclature proposed by Daniell deserves the preference. It has been described (p. 194) that Faraday proposed to term the elements which pass to the electrodes of the battery, *ions;* acting on this, Daniell proposes to term the electro-negative element of the sulphates, *oxysulphion;* that of the nitrates, *oxynitrion*, and so on, and the salts may be termed oxysulphion of copper, oxynitrion of sodium, &c. It would be desirable, however, for a long time, to introduce these names only where theoretical considerations rendered their employment decidedly useful, and hence, in all future description of the salts, I shall make use of the language of our ordinary views, and treat of their preparation and composition without any reference to the discussion in which we have been engaged.

The general adoption of the binary theory of salts has deprived of much of its interest and importance a question which some years since was very ingeniously discussed, viz., whether, in the formation of double salts, the salts which unite had the same relation to each other that the acid and base were then thought to have. Thus it was supposed that the electro-negative qualities of sulphuric acid being less controlled by oxide of copper than by potash, the alkaline sulphate acted as a base to the sulphate of copper when these two salts combined to form the double sulphate of potash and copper, and so on in other instances; but, in addition to the circumstance that all we have said as to the constitution of the salts militates against this view, we have the positive evidence that, first, these double salts are formed, not by combination merely, but by replacement of the constitutional water of the sulphates of the copper or magnesian class, which water nobody would contend to act in them as a base; and, second, that when a solution of such a double salt is decomposed by the battery, the two salts are not separated as if they were acid and base, but are decomposed independently in the proportions of an equivalent of each, making together the sum of the chemical energy of the current.

A similar idea was advocated by Bonsdorff regarding the double chlorides, iodides, &c. He proposed to consider the chlorides of gold, platina, mercury, &c., as chlorine acids, and those of potassium, &c., as chlorine bases, and so with the iodides. This view, however, although at first very extensively adopted, has given way to the gradual growth of knowledge. There is no analogy between a dry oxygen acid and a chloride; but the chlorides are in perfect analogy with the neutral salts. Thus Cu.Cl. does not resemble S.O_3, but Cu.S.O_4 and Cu.Cl.+K.Cl. are analogous, not to S.O_3.K.O., but to the double salt, Cu.S.O_4+K.S.O_4. Bonsdorff's idea was exactly counter to the direction of truth; he sought to bring all salts under the one head, by extending to all the constitution of oxygen acids and oxygen bases, while the progress of science has led us to the opposite generalization of reducing all salts to the simple haloid type.

CHAPTER XV.

SPECIAL HISTORY OF THE MOST IMPORTANT SALTS OF THE INORGANIC ACIDS AND BASES.

THE multitude of salts known to chemists is so very great, that it is only possible to detail the history of the most important of each class. They are arranged according to their bases, except in some few cases, where a metal is also the radical of their acid element. In that case, the salts of the acids of the metal are described after those formed by its oxides with other acids. This plan has been adopted in order to give as much unity as possible to the history of each metal, and influences only the compounds of chrome and arsenic to any degree.

Of the Salts of Potash.

Chloride of Potassium.—K.Cl. Eq. 932·6 or 74·7. This salt may be artificially produced by neutralizing potash with hydrochloric acid. It exists abundantly in the water of many brine springs, and in the ashes of plants. It is very soluble in water, producing so much cold as to be employed as a freezing mixture; it crystallizes in cubes, which are anhydrous; its principal use is in the manufacture of alum.

Iodide of Potassium.—K.I. Eq. 2069·4 or 165·8. A variety of processes may be employed to prepare this salt. One of the simplest consists in dissolving iodine in solution of potash until this is completely neutralized. The potash being decomposed, there is formed from 6I. and 6K.O., 5K.I. and K.O. . $I.O_5$. The solution is evaporated to dryness, and the mass being heated to redness, is kept fused as long as bubbles of oxygen gas are given off: the residual salt, which is pure iodide of potassium, is, when cold, to be dissolved in its weight of boiling water, and allowed to crystallize very slowly. A certain loss may occur in this process if the heat applied be too high, and if the temperature be not high enough, iodate of potash may remain undecomposed; this last effect being advantageous to the manufacturer by increasing the quantity of product, is more liable to occur, and may be detected by means of tartaric acid, as very ingeniously proposed by Mr. Maurice Scanlan. This acid is without action on pure iodide of potassium, farther than to liberate hydriodic acid, which remains for a certain time unaltered; but if a trace of iodate of potash be present, the iodic acid which is set free immediately reacts on the hydriodic acid, water being formed and iodine liberated, which may be recognised by means of starch.

Another process, adopted by the London and Edinburgh Pharmacopœias, consists in putting together iodine, metallic iron, and carbonate of potash; the iron and iodine unite directly to form a soluble iodide of iron, which is decomposed as rapidly as formed

by the carbonate of potash. Iodide of potassium is produced with oxide of iron and carbonic acid; a quantity of the latter combines with the oxide of iron, but as this is not pure protoxide, most of the carbonic acid is evolved as gas. The reaction consists in Fe.I. and K.O. . $C.O_2$, giving rise to K.I. and Fe.O. . $C.O_2$. The liquor being filtered and evaporated to a pellicle, the iodide of potassium is obtained crystallized. This salt crystallizes in cubes; sometimes in square prisms, which are macles. It is not deliquescent when pure, and is without action on turmeric paper; by this means it is known to be free from carbonate of potash. It is sometimes adulterated by chloride of potassium, which may be detected by decomposing its solution by nitrate of silver, washing the precipitate with water, digesting it in strong water of ammonia, and filtering; if the solution, when rendered slightly acid with nitric acid, give a white precipitate of chloride of silver, chloride of potassium was present, and its amount may be thus determined.

The iodide of potassium is extensively used in medicine, by the chemist as a reagent, and for the preparation of other metallic iodides.

A solution of iodide of potassium dissolves iodine in large quantity, forming a brown liquor used in medicine. It is not certain, however, that in this case any definite compound (as a biniodide) is formed.

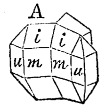
Bromide of Potassium.—K.Br. Eq. 1468·3 or 117·6. This salt may be prepared exactly as the iodide of potassium, which it resembles in most of its physical characters. It is recognised by giving, with oil of vitriol, orange-red fumes of bromine. The commercial article is frequently adulterated with chloride of potassium, the presence of which may be detected as follows: dissolve 100 grains of the salt in four ounces of water, and decompose it by an excess of nitrate of silver; collect the precipitate, wash it carefully, and dry it in a capsule till it ceases to lose weight; then weigh it. If it were perfectly pure, the bromide of silver should weigh 158·8 grains; but the presence of chloride of potassium would have the effect (from the smaller equivalent of chlorine) of increasing the weight; therefore, if the precipitate, when quite dry, weighs more than 158·8 grains, the sample is impure, and the quantity of chloride present may be calculated from the overplus weight, for 100 grains of pure chloride of potassium should give 192·6 grains of precipitate. Thus, if there were 10 per cent. of impurity, the precipitate would weigh 162 grains; if 20 per cent., it would weigh 165·4. Thus the precipitate increases in weight about 3·3 for each 10 per cent. of chloride of potassium present.

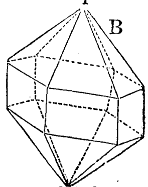
The properties of the *Fluoride* and of the *Silico-fluoride of Potassium* are not of importance beyond what has been already said in p. 321, 323, and 324.

Sulphate of Potash.—K.O. . $S.O_3$ Eq. 1091·1 or 87·43. This salt is produced upon the large scale in the manufacture of the sulphuric and nitric acids, where nitrate of potash is employed. It may be prepared by the direct union of its constituents, and, being but sparingly soluble, it precipitates as a fine crystalline powder when oil of vitriol is mixed with a strong solution of potash. It is more sol-

uble in boiling water, and crystallizes, on cooling, in right rhombic prisms, or in six-sided prisms terminated by pyramids, which are macles, being formed by the union of three simple crystals, as described in p. 28. In the figures, A represents the manner in which the three rhombic prisms adhere together, the letters marking the corresponding planes in each original, and B the form which results when all traces of the junctions have disappeared. This salt does not contain water; its crystals decrepitate violently when heated, but are not decomposed. 100 parts of water dissolve 8·3 of the salt at 32°, and 25 parts at 212°. This salt combines with dry sulphuric acid to form a bisulphate of potash, $K.O.+2S.O_3$, which may be prepared by exposing the neutral salt to the vapour of dry sulphuric acid, or by dissolving it with $1\frac{1}{2}$ equivalents of oil of vitriol in the smallest possible quantity of distilled water. This bisulphate of potash crystallizes in small prisms, which are gradually decomposed by water, the following salt being formed.

A





B

Common Bisulphate of Potash. Double Sulphate of Water and Potash.—$K.O..S.O_3+H.O..S.O_3$. Eq. 1704·7 or 136·6. This salt is produced when nitrate of potash is decomposed by two atoms of oil of vitriol, and is formed when neutral sulphate of potash is gently heated with half its weight of oil of vitriol to just below redness. It may be obtained crystallized from a strong solution in right rhombic prisms. It is decomposed into neutral sulphate and oil of vitriol by a large quantity of water. When heated to full redness, it fuses, and may be obtained, on cooling, in oblique rhombic crystals; it is thus dimorphous (see p. 227); at a higher temperature it abandons its excess of acid, and neutral sulphate remains.

There exists also a *hydrated sesquisulphate of potash*, $2(K.O..S.O_3)+H.O..S.O_3$, which crystallizes in fine needles. Similar compounds of sulphate of potash with hydrated nitric and phosphoric acids have also been described.

Nitrate of Potash. Saltpetre. Nitre.—$K.O..N.O_5$. Eq. 1266·9 or 101·5. The general principles of the formation of nitric acid by the conjoined action of decomposing animal matter and of earthy bases on atmospheric air, have been described already. By lixiviating the materials thus obtained, whether naturally or from artificial nitre beds, with water, a solution is obtained, containing, among other saline matters, a considerable quantity of nitrate of lime; this is then decomposed by an impure carbonate of potash, and carbonate of lime being precipitated, a solution of nitrate of potash is obtained, from which the salt is procured by evaporation and crystallization. Its form is that of a six-sided prism with dihedral summits, derived from the right rhombic system. It is anhydrous; 100 parts of water dissolve 13·3 parts at 32°, and 240 parts at 212°; when heated to redness, it melts and evolves oxygen, at first pure, but subsequently mixed with nitrogen gas.

As nitrate of potash contains oxygen in large quantity, and gives it out readily to combustible bodies, it is much employed for the preparation of fireworks, and especially of gunpowder. The action of gunpowder depends upon its generating, when decomposed, a large quantity of gases, which occupy more than 1000 times its vol-

ume. If this took place instantaneously, all bodies near, which could not resist this force, would be burst or broken; as takes place with chloride of azote, which, if placed in a gun, would burst it, but have no power to propel a ball; the decomposition of gunpowder, however, occupying a certain time, the disengagement of gas is progressive, and the ball is forced through the barrel with the velocity due to the ultimate effect of the whole quantity of gas produced. When gunpowder is completely decomposed, the products are found to be sulphuret of potassium, nitrogen, and carbonic acid gas, and from these the proportions by weight of its constituents may be calculated, for S., K.O. . $N.O_5$, and 3C., produce K.S., N., and $3C.O_2$. The parts by weight are, therefore,

	Theory.		French.	English.	Prussian.
S.=	16·1	— 11·8	12·5	10·0	11·5
3C.=	18·3	— 13·5	12·5	15·0	13·5
K.O. . $N.O_5$=	101·5	— 74·7	75·0	75·0	75·0
	135·9	100·0	100·0	100·0	100·0

The proportions employed in the government factories of the most important countries are given also above. The Prussian mixture agrees best with theory. For the coarse blasting powder, there are employed sixty-five parts of saltpetre, twenty of sulphur, and fifteen of charcoal. The excess of sulphur renders the explosion more intense, but would corrode firearms too much. A mixture of three parts of saltpetre, four of carbonate of potash, and one of sulphur, is decomposed instantaneously when fused, and with an explosion so violent, that, if it be placed on a thin iron plate, it may be perforated. If three parts of nitre be mixed with one of finely-powdered charcoal, a mass is obtained which, when touched with an ignited coal, burns nearly as fast as loose gunpowder, but totally without explosion. It is therefore the sulphur which determines the violence and rapidity of the deflagration of gunpowder, while the charcoal produces the great volume of gas on which its mechanical effect depends.

The preparation of the materials for making gunpowder requires great care. Most of the success depends on the preparation of the charcoal. This should be made from a light wood containing little ashes, such as birch, and carbonized in cylinders, very slowly, and at the lowest possible heat. When reduced to impalpable powder, this charcoal is so inflammable as sometimes to take fire at ordinary temperatures. The purification of the saltpetre is performed by successive recrystallizations, and by washing the crystals with water already saturated with saltpetre, which dissolves out any common salt that may be present, but does not act on the crystals of saltpetre. The description of the mechanical operations of the manufacture would be out of place here.

Hypochlorite of Potash.—When gaseous chlorine is passed into a solution of carbonate of potash, it is abundantly absorbed, but no carbonic acid is disengaged until the liquor contains an atom of chlorine for every two atoms of alkaline carbonate. On examination, it is then found to contain hypochlorite of potash, chloride of potassium, and bicarbonate of potash, which are mixed in solution, and may be partially separated by crystallization. The reaction has been such that 2Cl. and 4K.O. . C. O_2 give K.Cl., K.O. . Cl.O., and $2(K.O.+C.O_2+H.O. . C.O_2)$. If the stream of chlorine be continued, carbonic acid is copiously evolved, and as much more chlorine is absorbed, giving ultimately a mixture of K.Cl. and K.O. . Cl.O. The liquor becomes deep yellow, owing to the liberation of a quantity of hypochlorous acid by the free carbonic acid, and hence the quantity of chlorine absorbed amounts to much more than the exact atomic proportion.

Farther details of the theory of these bleaching compounds are given under the head of chloride of lime.

Chlorate of Potash.—K.O. . $Cl.O_5$. Eq. 1532·6 or 122·81. When chlorine gas is passed into a strong solution of potash, it is absorbed rapidly until the alkali is completely neutralized, and chloride of potassium and hypochlorite of potash are formed; 2K.O. and 2Cl. giving K.Cl. and K.O. . Cl.O. If, then, this liquor be boiled for some time, oxygen gas is given off, the hypochlorite being decomposed, and chloride of potassium and chlorate of potash being formed; 9(K.O. . Cl.O.) producing 12O. with 8K.Cl. and K.O. . $Cl.O_5$. If carbonate of potash has been employed, the absorption of the chlorine is rapid until half of the salt has been decomposed and the remain-

der converted into bicarbonate, from combining with the evolved carbonic acid, as described under the preceding head; but a high temperature and a great excess of chlorine being necessary to complete the reaction, render the operations tedious and very troublesome; and as, owing to the large quantity of oxygen evolved, there is but one equivalent of chlorate of potash obtained by the action of eighteen equivalents of chlorine on eighteen of potash, the process is one of considerable expense.

We owe to Graham a method which is free from these disadvantages. If an equivalent of carbonate of potash be mixed with one of hydrate of lime (by weight about 2 of K.O. . C.O to 1 of Ca.O. . H.O.), and exposed to a current of chlorine, the gas is absorbed with avidity, and the solid mass becomes very hot, while water is given off abundantly. When saturated, it may be gently heated to complete the decomposition. No oxygen is given off, the reaction being that 6(K.O. . $C.O_2$) and 6(Ca.O. . H.O.), acted on by 6Cl., produce 5K.Cl., 6Ca.O. . $C.O_2$, and K.O. . $Cl.O_5$, while 6H.O. are evolved. By digesting the mass in water, the potash salts are dissolved out, carbonate of lime remaining, and the chlorate of potash may be separated from the chloride of potassium by crystallization. By this means three times as much product may be obtained from the same materials as by the older process.

This salt crystallizes in rhomboidal tables of a pearly lustre: it is anhydrous: 100 parts of water dissolve but 3·5 parts at 32°, and 60 parts at 219°. It tastes sharp and cooling, like nitre; when heated, it melts and evolves oxygen gas, being decomposed into chloride of potassium and hyperchlorate of potash; on increasing the heat, this also is decomposed, and chloride of potassium remains pure. Its uses in preparing oxygen, and the compounds of chlorine and oxygen, have been already noticed. From its supplying oxygen still more readily than nitre, it is the basis of a variety of deflagrating mixtures. When rubbed in a mortar with sulphur or with sulphuret of antimony, it explodes violently. Placed in contact with a minute bit of phosphorus on an anvil, and struck by a hammer, it gives a dangerous detonation. The ordinary lucifer matches are formed by mixtures of chlorate of potash with sulphur and charcoal, or sulphuret of antimony or of cinnabar, made into a paste with gumarabic, and applied to the extremity of a bit of stick, previously smeared with sulphur. Students should be very cautious how they employ this salt in such experiments as those now noticed.

Perchlorate of Potash—K.O. . $Cl.O_7$; Eq. 1732·6 or 138·8—is of importance only from being one of the least soluble salts of potash, and, consequently, that the perchloric acid may be used as a test for the presence of potash in solution, it giving a granular crystalline precipitate if that alkali be present. Its preparation is sufficiently noticed in page 306.

The *Silicate of Potash* is of considerable importance as a constituent of glass, and will be noticed as such hereafter.

Iodate of Potash.—K.O. . $I.O_5$. This salt, which is but sparingly soluble in water, may be obtained by neutralizing the perchloride of iodine with caustic potash; I. Cl_5 and 6K.O. produce 5K.Cl. and K.O. . $I.O_5$. This last separates in crystalline grains. It may also be obtained by adding iodide of potassium to fused chlorate of potash; the mass froths up, the oxygen passing to the iodine, and there is obtained a mixture of chloride of potassium and iodate of potash, which may be separated by crystallization. This salt has a remarkable tendency to form acid and double salts, of which, however, none are specially interesting.

Salts of Sodium.

Chloride of Sodium. Common Salt. Sea Salt—Na.Cl.; Eq. 733·6 or 58·8—exists in great abundance in nature; solid, as *rock salt*, and in solution in the water of the ocean, and of many inland seas and lakes. The deposites of rock salt occur only among the more recent (secondary) geological formations, lying above the coal, and in connexion with the new red sandstone, as in Cheshire. The beds of salt are sometimes of great magnitude; thus, at Northwich, the bed now worked is supposed to be not less than 60 feet thick, a mile and a half long, and 1300 yards wide; and the deposites at Wieliczka, in Poland, appear to be still larger. The origin of these deposites of salt is probably to be found in the gradual drying up, by evaporation, of salt lakes, to which fresh quantities of salt were continually supplied by the surrounding springs. Owing to admixture of earthy matters, the rock salt, as quarried, is generally brownish-coloured, and hence requires to be dissolved in water and crystallized for use. The expense of extracting the salt may be in many cases lessened, by simply boring down to the bed with a pipe a few inches in diameter, and letting thereby water run in upon the salt; a strong solution of salt is thus produced, which is pumped up and evaporated. The expense of sinking a shaft and quarrying out the solid salt is thus avoided.

In warm countries, as on the coasts of Portugal and of the south of France, salt is obtained by the spontaneous evaporation of sea-water, which is allowed, on the rise of the tide, to flow into shallow basins, being passed from one to another, according as it becomes more concentrated, and, finally, the evaporation being finished by means of artificial heat. The sea-water is not evaporated to dryness, as its other saline ingredients would in that case be mixed with the common salt. The sea-water is generally composed of

Chloride of sodium	2·50	100·00,
Chloride of magnesium	0·35	
Sulphate of magnesia	0·58	
Carbonate of lime and Carbonate of magnesia	0·02	
Sulphate of lime	0·01	
Water	96·54	

with generally some traces of iodide and bromide of magnesium. According as the evaporation proceeds, the common salt is deposited in crystals, and the mother liquor, or *bittern*, being rich in salts of magnesia, is preserved for the manufacture of Epsom salts.

In addition to these sources, chloride of sodium may be obtained by the direct combination of its elements, or by decomposing carbonate of soda by muriatic acid. In practice, however, this is never done.

Chloride of sodium crystallizes in cubes. Its taste is purely saline. It is equally soluble in water at all temperatures, 100 of water dissolving 36·5; by a very strong heat it may be volatilized. Its crystals are anhydrous, but are generally fissured, containing water, which, when heated, bursts the crystal, producing loud de-

crepitation. A strong solution of salt does not freeze at 0°, but deposites crystals in rhombic plates, which are a hydrated chloride of sodium. If these crystals be heated beyond 15° they give out water, and are changed into minute cubes.

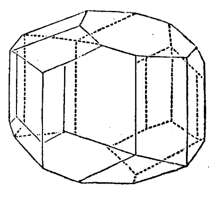
The uses of chloride of sodium are very numerous and important. Besides being employed in seasoning food, it is now universally the source from whence the other compounds of sodium, such as the carbonate and sulphate, are obtained. It is employed also in the manufacture of glass and of porcelain, and as a manure.

The *bromide and iodide of Sodium* resemble, in properties and mode of preparation, the corresponding compounds of potassium, and do not require special notice.

Sulphate of Soda. Glauber's Salt.—Na.O..$S.O_3$+10 Aq. Eq. 892·1 +1125 or 71·48+90. So named after its discoverer: exists in some mineral waters, and may be prepared by neutralizing carbonate of soda by dilute sulphuric acid. For the purposes of commerce, it is manufactured in great quantities from common salt, as described under the head of muriatic acid (p. 307).

As it is not the object of the process to economize the muriatic acid gas, the decomposition is carried on in a reverberatory furnace similar to that figured in p. 333. Three or four hundred weight of salt being spread over the floor of the furnace, forming a layer three or four inches deep, the equivalent quantity (an equal weight) of sulphuric acid, of the strength 1·600, as taken from the chambers, is poured in through an aperture in the dome, and a moderate fire kept up until the materials begin to dry; the fire is then increased gradually until all the muriatic acid gas has been expelled, and the residual sulphate of soda begins to fuse. The acid gas passes up the chimney, and is either allowed to pass away into the air, or is condensed by meeting with a stream of water, and the weak liquid acid thus formed is suffered to run to waste. The greater part of the sulphate of soda thus produced is immediately used to make carbonate of soda; but to form Glauber's salt, it is only necessary to dissolve it in warm water, and let it crystallize by cooling.

The sulphate of soda crystallizes in six-sided prisms, as in the figure, very much channelled at the sides. It is easily soluble in water, having a point of maximum solubility at 93°, as figured in page 22. Its ordinary crystals contain 56 per cent. of water; by exposure to the air it loses all its water by efflorescence, and falls into a white powder; from a hot saturated solution opaque rhombic octohedral crystals are deposited, which are anhydrous.



The isomorphism of these crystals with permanganate of barytes, and the speculations founded on it, have been noticed p. 224. A *bisulphate* and a *sesquisulphate of Soda* may be formed by adding oil of vitriol to a solution of the neutral salt, and crystallizing by evaporation. They are much less determinate than the acid sulphates of potash.

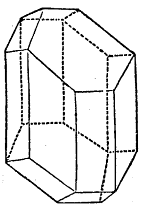
Nitrate of Soda. Cubic Nitre.—Na.O..$N.O_5$. Eq. 1067·5 or 85·57. The spontaneous formation of this salt by the atmospheric influence, probably on a soil containing chloride of sodium, has been noticed

p. 277. It may also be obtained by means of nitric acid and carbonate of soda. It crystallizes in rhombs, isomorphous with calc spar (p. 224). It is very soluble in water, and is slightly deliquescent; hence it cannot be employed in the manufacture of gunpowder. It is used for the manufacture of nitric and sulphuric acids, and as a manure.

Hyposulphite of Soda.—Na O. . S_2O_2+10 Aq. This salt, which has become of some practical interest, from its use in dissolving off the sensitive silver compounds in making photogenic drawings, may be made by boiling together three parts of dry carbonate of soda with one of sulphur until this last is dissolved, and then passing a stream of sulphurous acid gas through the liquor until it smells strongly of it. Na.O. . $C.O_2$, with S. and $S.O_2$, produce Na.O. . S_2O_2, while $C.O_2$ is evolved. If the three parts of carbonate of soda be boiled with two of sulphur, and the deep yellow liquor be exposed to the air until it yields a colourless liquor on filtration, the salt is more simply produced, the necessary quantity of oxygen being absorbed from the air. The hyposulphite of soda thus formed is easily soluble in water. Its resemblance to Glauber's salt in form, and its other properties, are noticed in p. 291.

Hypochlorite of Soda. Chloride of Soda. Disinfecting Liquor of Labaraque—Is produced by treating a solution of carbonate of soda with chlorine as long as this is absorbed, but no carbonic acid evolved. For farther observations, see the hypochlorites of potash and of lime.

A. *Tribasic Phosphate of Soda.*—The common phosphate of soda of the shops is a tribasic salt, containing ($P.O_5$+2Na.O.+H.O.)+24 Aq. It is prepared by decomposing the solution of acid tribasic phosphate of lime obtained from bones (as described in p. 295) by means of carbonate of soda. Carbonate of lime is thrown down, and phosphate of soda formed. It is easily soluble in water, and crystallizes in oblique rhombic prisms, as in the figure, which react alkaline. When exposed to the air, it loses some of its water by efflorescence (ten atoms ?), but the crystals retain their form. If this salt be mixed with an excess of caustic soda, the atom of basic water is displaced, and the subphosphate of soda ($P.O_5$+3Na.O+24 Aq.) crystallizes in long prisms; and by the addition of hydrated phosphoric acid to its solution, and cautious evaporation, the acid tribasic phosphate ($P.O_5$+Na.O.+2H.O.)+2 Aq., which crystallizes in oblique rhombic prisms, is formed: it is dimorphous.



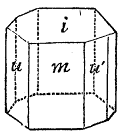
The characteristic of these three salts is to give with nitrate of silver a yellow precipitate of tribasic phosphate of silver.

B. *Bibasic Phosphate of Soda.*—Of these salts, that termed the *Pyrophosphate of Soda*,($P.O_5$+2Na.O.)+10 Aq., is of interest, as its discovery led the way to the true history of these bodies. It is formed by fusing the common phosphate of soda, ($P.O_5$+2Na.O.+H.O.) +24 Aq., at a red heat. All the water of crystallization is given off at a very moderate heat; but by a red heat the twenty-fifth or basic atom is expelled, and, when the salt is then redissolved, the phosphoric acid does not recombine with basic water, but remains

united only with the soda. It is recognised by giving a white precipitate with nitrate of silver.

C. *The Monobasic Phosphate of Soda*, $P.O_5 + Na.O.$, is obtained by heating the acid tribasic or bibasic phosphates of soda to redness. All the volatile base being thus expelled, the phosphoric acid remains combined with one equivalent of soda. This salt fuses into a transparent glass; is deliquescent; its solution does not crystallize. It is easily recognised by throwing down from solutions of lead and silver, precipitates, which are not powders, but soft, tenacious pastes.

Borates of Soda.—Boracic acid combines with soda in many proportions, forming salts, of which the most important is the *biborate*, the *borax* of commerce $(Na.O. + 2B.O_3) + 10$ Aq. It exists in the water of several lakes in Thibet and China, also in Hungary, and was imported thence in small crystals, smeared with a fatty matter, under the name of *tinkal*. The borax of commerce is now obtained by treating the native boracic acid obtained from Tuscany, p. 326, by carbonate of soda. On the application of heat, the acid dissolves with the evolution of carbonic acid and ammonia; the liquor is run into large vats lined with lead, where it cools very slowly, and the borax gradually crystallizes in oblique rhombic prisms, as *i*, *u*, *m*, in the figure. If a strong solution of borax be kept at 33°, the salt crystallizes in regular octohedrons with only five atoms of water. Although this salt contains two equivalents of acid, it has an alkaline reaction: when heated, it froths up very much, abandoning its water. The dry salt melts at a red heat into a colourless glass, which dissolves most metallic oxides very readily, and hence is serviceable in experiments with the blowpipe, as enabling the metals to produce the coloured glasses by which they are recognised; under the head of glass and porcelain, its use in these branches of art will be again noticed.



The remaining compounds of boracic acid with soda, as the neutral borate, $Na.O.\,.\,B.O_3 + 8$ Aq., and acid salts, as $Na.O. + 4B.O_3$ and $Na.O. + 6B.O_3$, are not important.

Silicate of Soda will be described under the head of glass.

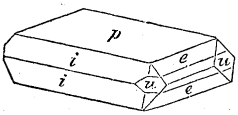
Salts of Lithium.—From the rarity of this body, its salts require no farther notice than that its carbonate is but very sparingly soluble in water, yet its solution possesses an alkaline reaction. It thus serves to connect the alkaline with the earthy bases.

Salts of Barium.

Chloride of Barium.—$Ba.Cl. + 2$ Aq. Eq. $1299{\cdot}6 + 225$ or $104{\cdot}8 + 18$. This salt may be prepared by decomposing the native carbonate of barytes with dilute muriatic acid, or, more economically, by decomposing the sulphuret of barium, the preparation of which is described in p. 342, by dilute muriatic acid. In the former case, carbonic acid, in the latter, sulphuretted hydrogen, is given off The chloride of barium crystallizes from a hot solution in rhomboidal tables which contain 14·7 of water.

Sulphate of Barytes.—$Ba.O.\,.\,S.O_3$. Eq. 1458 or 119·5. This salt exists native, in great abundance, being the most common source of barytes. It is very generally associated with sulphuret of lead,

and serves as an indication of the probable proximity of that ore. It is totally insoluble in water. Its crystalline form is an oblique rhombic prism, generally very flat, as in the figure; derived from an octohedron of which *i* and *e* are planes; the secondary planes, *p* and *u*, belong to the prism. It is one of the heaviest of saline bodies, its specific gravity being 4·3; hence its name of *heavy spar* and *terra ponderosa*. When ground to fine powder, it is used as a cheap substitute for white lead in painting, for which large quantities of it are employed; but its crystalline texture prevents it having the opacity or *body* necessary in a good pigment. It may be prepared artificially by adding sulphuric acid to any solution containing barytes; it falls as a heavy white crystalline powder. Its total insolubility renders its constituents excellent reagents for each other.



Nitrate of Barytes—$Ba.O.+N.O_5$; Eq. 1633·9 or 130·9—may be produced by acting on carbonate of barytes with dilute nitric acid, or, more cheaply, by mixing strong hot solutions of sulphuret of barium and nitrate of soda. The sparingly soluble nitrate of barytes crystallizes as the mixed liquors cool, but the sulphuret of sodium remains dissolved. In this process, from Ba.S. and $Na\,O.\,.\,N.O_5$ we obtain $Ba.O.\,.\,N.O_5$ and Na.S. This salt requires twelve parts of cold water for solution, but dissolves in four of boiling water, from which it crystallizes on cooling in octohedrons. These crystals are anhydrous. When heated, they yield pure barytes.

The other salts of barytes do not require notice.

Salts of Strontium.

Chloride of Strontium.—Sr.Cl. + 6 Aq. Eq. 989·9 or 79·32. This salt is obtained from the native carbonate or sulphate of strontia, exactly as chloride of barium is obtained from the native salts of barytes. It crystallizes in long needles which deliquesce. It is very soluble in water.

Sulphate of Strontia.—$Sr.O.\,.\,S.O_3$. Eq. 1148·4 or 91·9. This, the most abundant source of strontia, is found native crystallized, isomorphous with sulphate of barytes. It may be produced artificially as a white powder, by adding sulphuric acid to any solution containing strontia. It is dissolved by 3600 parts of boiling water, and remains dissolved after cooling. It is fused by a strong heat; with charcoal it gives sulphuret of strontium.

Nitrate of Strontia—$Sr.O.\,.\,N.O_5$—crystallizes in octohedrons, which dissolve in five parts of cold, and one half part of boiling water. Mr. Scanlan has observed, that during the crystallization of this salt bright flashes of light are emitted. It is anhydrous, but decrepitates when heated, owing to mechanically included water. On the application of heat, these crystals evolve oxygen and nitrogen, and leave pure strontia.

Salts of Calcium.

Chloride of Calcium—Ca.Cl. + 6 Aq.; Eq. 698·7 + 675 or 55·98 + 54—is obtained by decomposing carbonate of lime with muriatic acid. In the laboratory it is abundantly procured as the residue of

the preparation of carbonic acid, ammonia, &c. It is very soluble in water; its solution, evaporated to the consistence of a sirup, gives, by cooling, long, striated, rhombic prisms, which deliquesce with great rapidity, and when heated undergo watery fusion, soon after which it abandons two thirds of its water of crystallization, and a powder is obtained, Ca.Cl.+2 Aq., in which form it is best adapted for freezing mixtures. Heated still farther, it becomes anhydrous, and at a red heat fuses. In this state it is phosphorescent in the dark, forming Homberg's pyrophorus. It has a very great affinity for water, combining with two atoms of it, with the evolution of much heat, and is hence employed to dry gases for experimental purposes, and to remove water from liquids, as in the rectification of alcohol.

This salt combines with lime, forming an oxychloride of calcium, Ca.Cl.+3Ca.O., which is obtained by boiling a solution of it with an excess of lime, and filtering. The new substance crystallizes, on cooling, in small flat rhombs, which contain forty-nine per cent., or fifteen atoms of water.

The *bromide* or *iodide of Calcium* do not present any interest.

Fluoride of Calcium, Ca.F., is an abundant mineral known as *fluor spar*, found crystallized in cubes and octohedrons, but principally massive. When first extracted from the earth it is moderately tough and soft, and is cut into ornaments, which present a beautiful variety of colours. Its crystals become strongly phosphorescent by heat or by electricity. It is insoluble in water; from it all the other preparations of fluorine are derived, as noticed in p. 319, 324, and 327. It appears as a gelatinous precipitate when hydrofluoric acid is added to any soluble salt of lime. When heated in contact with silicious or aluminous minerals, it forms easily fusible compounds, and being thus of use as a *flux* in the smelting of metallic ores, its name of *fluor spar* was thence derived.

Sulphate of Lime—Ca.O. . $S.O_3$+2 Aq.; Eq. 857·2+225 or 68·69+18—may be prepared artificially, by mixing a solution of any soluble salt of lime with sulphuric acid. It forms a crystalline powder, nearly equally soluble in hot and cold water, requiring 461 times its weight for its solution. It occurs in nature abundantly, and in various forms: 1st, in distinct colourless crystals; 2d, in semi-transparent masses of crystalline structure, constituting *alabaster*, and in amorphous masses, forming extensive rocky strata, in many places, in which state it is called *common gypsum*. From this *plaster of Paris* is prepared, by calcining the gypsum, broken into small pieces, in ovens at a temperature below 300°, until its water of crystallization is expelled. In this operation it falls to powder, and is to be put up in tight vessels so as to exclude the air. When mixed with water it rapidly recombines with the two atoms, evolving heat and expanding in becoming solid, so as to fill up all interstices of the mould into which it may be poured. On this property is founded the art of casting in plaster and the formation of the various kinds of *stucco*, or *artificial stone*, in which a solution of glue, or of various earthy salts, may be substituted for pure water. If the gypsum be heated, in baking, above 300°, it is changed in nature, and no longer combines with water so as to set; it is then converted into a form which exists in nature crystallized, and which is termed *anhydrite*.

A double salt of sulphate of lime and sulphate of soda is found native, and termed Glauberite. It is insoluble in water, by which it is also decomposed. It cannot be formed artificially.

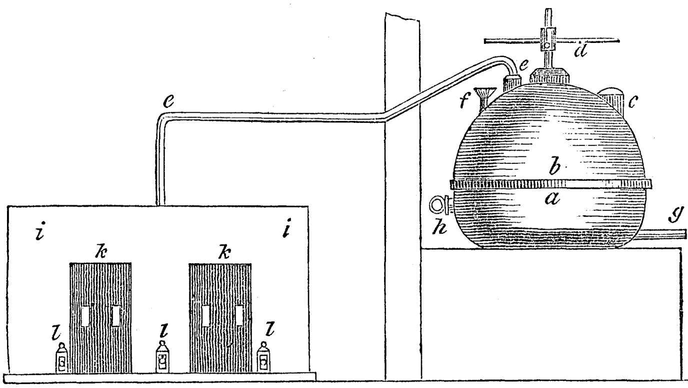
The *Hyposulphite of Lime* is a soluble salt, the mode of preparing which is described p. 291.

The *Nitrate of Lime* is very deliquescent, and is decomposed by a moderate heat.

Phosphoric acid combines with lime in several proportions, of which the most important is the *Basic tribasic Phosphate of Lime*, or *Earth of Bones*. This salt, which constitutes the inorganic portion of the skeletons of the mammalia, mixed only with small quantities of carbonate and sulphate of lime, and of fluoride of calcium, has the formula $8Ca.O. + 3P.O_5$. It may be obtained precipitated by dissolving bone earth in muriatic acid, and exactly neutralizing the solution by caustic ammonia. It falls as a gelatinous powder containing four atoms of water. As the phosphoric acid of bones is in its tribasic condition, Graham considers it to be a combination of two phosphates, thus, $2(3Ca.O. . P.O_5 + Aq.) + (H.O. . 2Ca.O. . P.O_5 + Aq.)$. Each of these tribasic phosphates of lime may be obtained separate, by decomposing solutions of chloride of calcium by solution of the ordinary phosphate, or of the subphosphate of soda.

Hypochlorite of Lime. Chloride of Lime. Bleaching Salt.—When speaking of the oxygen compounds of chlorine, and of the chlorate and hypochlorite of potash, I have had occasion to notice the diversity of opinion regarding the nature of the bleaching substances formed by the action of chlorine on the alkalies and on lime. Of these the chloride of lime is by far the most important in the arts

It is prepared by generating chlorine in a large still, *a*, *b*, *h*, *f*, as described p. 301 the materials being kept constantly mixed by means of an agitator moved round by the handle *d*. The gas is conducted by the tube *e e* to the upper part of a wooden reservoir or apartment, as in the figure, made very tight, *i*, *i*, on the floor



of which pure hydrate of lime is exposed to the action of the gas. The lime is introduced by the door *k*, *k*, and the surface is changed occasionally by stirring with rakes by means of the apertures *l*, *l*, *l*: the absorption should take place so slowly as not to evolve any sensible heat. In this way 100 parts of slacked lime combine generally with from fifty to sixty of chlorine. If the process be carried on too rapidly, a quantity of lime is decomposed, chlorate of lime and chloride of calcium being formed, which may be recognised by the product getting damp when exposed to the air

The best bleaching powder thus prepared by the dry way does not contain more than forty per cent. of chlorine; this does not correspond to any exact atomic constitution; but if lime be diffused through water so as to form a thin cream, it then absorbs more than its own weight of gas, and is totally dissolved. It is probably the mechanical disadvantages of the dry way which prevents the absorption of the gas reaching this limit, and the best bleaching powder may be looked upon as a mixture of true chloride of lime, with about eighteen per cent. of hydrate of lime in excess. Accordingly, when ordinary bleaching powder is treated with water, the true atomic compound is dissolved out, and the excess of lime remains. The composition of the theoretical and best practical substances may, therefore, be expressed as follows:

Theoretical.				Best practical.	
1 atom chlorine,	35·47	48·63		Chlorine	40·32
1 " lime,	28·57	39·04		Lime	45·40
1 " water,	9·00	12·33		Water	14·28
	73·04	100·00			100·00

But the generality of good samples in commerce will be found not to exceed thirty per cent. of chlorine.

The solution of this chloride of lime has a marked alkaline reaction; it is without any bleaching power except an acid be present, which liberates chlorine, and enables it to destroy the colouring matter. It is thus that the colour can be removed from certain points without injuring others, which is of very great importance in calico printing; thus a piece of cloth being dyed uniformly with madder (as Turkey red), the pattern is printed on with tartaric acid thickened with gum, and the whole being immersed in a bath of chloride of lime, the chlorine is liberated by the acid at every point of the pattern, and the cloth is there bleached, giving a white ground, on which other colours may be applied, while the general surface remains deep red. A solution of bleaching powder in water exhales a sensible odour of chlorine, owing to the absorption of carbonic acid from the air, and obtains thereby weak bleaching properties.

As the technical value of bleaching powder depends on the total quantity of chlorine which it contains, this may be determined without reference to its theoretical constitution. For this purpose a variety of methods have been proposed, and the process is termed *Chlorometry.* The earliest method employed consisted in preparing a standard solution of sulphate of indigo, which, being of a deep blue colour, was bleached by the chlorine expelled from the lime by the sulphuric acid, and evidently, the richer the bleaching powder was in chlorine, the more solution of indigo a certain weight of it could bleach. The action of chlorine on indigo is, however, so complex, that this method was found exposed to numerous fallacies, and may be considered as now obsolete. Latterly, Gay Lussac has proposed to substitute for this the more definite action of chlorine in acidifying arsenic. He prepares a solution of arsenious acid in muriatic acid, and dilutes this with water. On adding thereto a solution of chloride of lime, the muriatic acid takes the lime, and the chlorine, decomposing water, converts the arsenious acid into arsenic acid, and itself forms hydrochloric acid; $As.O_3$ with 2Cl. and 2H.O. producing $As.O_5$ and 2H.Cl. The proportions which I employ in this reaction are as follows: 100 grains of arsenious acid are to be dissolved in 2000 grains of strong spirits of salt, and this liquor diluted with distilled water till it occupies the volume of 7000 grains of water. This is the standard test liquor; to employ it, 100 grains of the bleaching powder to be tested are to be diffused through 1000 grains of water, and the test liquor to be gently poured from a graduated glass on it, in a deep jar, continually stirring the mixture. A drop of weak solution of sulphate of indigo is to be occasionally applied, by means of a glass rod, to the surface of the liquor; as long as any chlorine remains unaltered, the blue colour of the drop is instantly destroyed, and the addition of the arsenic liquor is to be continued until the blue drop remains unaltered. Then the quantity of chlorine present in the 100 grains of bleaching powder is represented by $\frac{1}{100}$th of the quantity of the test liquor employed; thus, if there were 2565 grains of the test liquor necessary to destroy the bleaching power of the 100 grains of chloride of lime, the quantity of chlorine would be 25·65. This is not absolutely correct; for in theory, the true quantity of chlorine indicated would be 26·08; but as a few drops of the solution are always employed, more than what should by theory be necessary, the practical proportion of $\frac{1}{100}$th comes very close to the truth. Even one half part per cent., which is the limit of error, is quite unimportant in practice.

Another method, which is simple and rapid in execution, is nearly the same as that described in p. 355 for determining the technical value of black oxide of man-

ganese by means of copperas (green sulphate of iron). The proportion and method of testing which I employ are as follows: 390 grains of clean and dry crystals of green sulphate of iron are to be dissolved in as much water as will bring the solution to the volume of 5000 grains of water. On the other hand, 100 grains of the chloride of lime are to be diffused through 1000 grains of water, and the solution of copperas is to be added thereto, until the presence of a trace of the protosulphate of iron in excess is indicated, by the mixed liquor striking a full blue colour when a drop of it is placed on a slip of paper, imbibed with red prussiate of potash. The quantity of chlorine present in the 100 grains of the bleaching powder is $\frac{1}{100}$th of the quantity of the standard copperas liquor employed; thus, if 2783 grains measure of the volume of the solution be found necessary, the sample contains 27·83 of chlorine per cent. For the 27·83 of liquor contains 217 grains of sulphate of iron, which is peroxidized by the action of 27·6 grains of chlorine; here, also, the limit of error need not exceed one half per cent. Other processes have been proposed, founded, some on the change of yellow prussiate into red prussiate of potash, by means of the chlorine of the bleaching powder; and others, by decomposing the bleaching powder by means of an excess of water of ammonia, and measuring the nitrogen gas evolved; but these are more troublesome and less exact than the processes already detailed, which are those most worthy of confidence from the manufacturer.

As to the theoretical nature of bleaching powder, chemists are not as yet able to decide positively. The original and simple idea of a direct combination between the chlorine and the lime has been revived by Millon, who advanced that, by decomposing the salts of lead, iron, and copper by solution of chloride of lime, precipitates were obtained, which were compounds of the protoxide of the metal united with as much chlorine as was equivalent to the oxygen necessary to form peroxide. Thus, that with lead, a chloroxide Pb.O.Cl.; that with iron, a chloroxide Fe_2O_2Cl. The chloride of lime, Ca.O.Cl., would thus be equivalent to deutoxide of calcium, Ca.O.O. It has been found, however, that the evidence is not yet satisfactory. The peroxide of potassium is $K.O_3$, while chloride of potash is not $K.O.Cl_2$, but K.O.Cl. The composition of all these bleaching compounds appears to be an atom of chlorine united to an atom of a protoxide, and this may be explained by supposing a hypochlorite and a metallic chloride to be formed; thus 2Ca.O. and 2Cl. may give Ca.O.+Cl.O. and Ca.Cl. But, if this happens, the chloride of calcium certainly remains combined, forming a double salt; for the bleaching powder, if properly prepared, has no tendency to deliquesce, and only becomes damp when long kept; and then chlorate of lime and free chloride of calcium are formed, and all its bleaching qualities are lost. There are thus two views equally tenable: first, that the bleaching compounds are *chlorides of oxides*, corresponding to peroxides; and, second, that they are double salts of a hypochlorite with a chloride; but there is no reason to consider that the chlorous acid, $Cl.O_4$, comes into play in their manufacture, although the salts of that acid, when otherwise prepared, do possess bleaching properties.

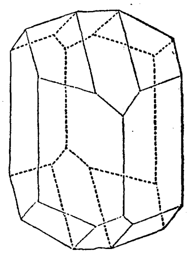
Salts of Magnesium.

Chloride of Magnesium—Mg.Cl.; Eq. 600·9 or 48.16—may be obtained in solution by acting on the carbonate of magnesia with muriatic acid; by evaporation, it may be obtained in prisms with 6 Aq., which are very deliquescent. These crystals cannot be deprived of water without total decomposition, the chlorine passing off as muriatic acid, and magnesia remaining behind. The chloride may, however, be obtained anhydrous, by previously mixing its so-

lution with sal ammoniac, with which it forms an anhydrous double salt, which, when heated to redness, gives off sal ammoniac, and the pure chloride of magnesium remains melted, and forms a clear crystalline mass when cold. The chloride of magnesium exists in sea-water.

Sulphate of Magnesia.—Mg O. . S.O_3. Eq. 759·4 or 50·8. This salt exists abundantly in saline mineral springs, as those of Seidlitz, Selters, and Epsom, from whence it derives its common name of *Epsom salt.* It is extracted principally from the magnesian limestone, which is calcined, and the mixed lime and magnesia treated with dilute sulphuric acid; the sulphate of lime, being very sparingly soluble, is easily separated from the sulphate of magnesia by washing with water; the latter is dissolved out, and the liquor evaporated and crystallized. A great deal is also made from the mother liquor of sea-water, or *bittern* (p. 426). This is decomposed by sulphuric acid, and the salt formed separated by crystallization.

The sulphate of magnesia crystallizes in eight rhombic prisms, as in the figure, containing seven atoms of water, of which one is constitutional, and the other six crystalline; its formula is therefore Mg.O. . S.O_3. H.O. + 6 Aq.; when heated to 212° it easily abandons the 6 Aq., but retains the seventh atom of water even at 400°. It combines with the sulphate of potash to form a double salt, (Mg.O. . S.O_3 + K. O. . S.O_3) + 6 Aq., the atom of constitutional water being replaced by the alkaline sulphate. The sulphates of soda and of ammonia act in the same way.



Nitrate of Magnesia. Mg.O. . N.O_5, is very soluble and deliquescent. It cannot be obtained dry, as it crystallizes with six equivalents of water, of which five are expelled by a moderate heat, and by a higher temperature the nitric acid itself passes off, and magnesia remains behind; Mg.O. . N.O_5. H.O. producing Mg.O. and H.O. . N.O_5.

The *Borate of Magnesia* constitutes the mineral boracite, whose electrical and crystalline properties have been already noticed.

There exists a great number of combinations of silicic acid with magnesia, constituting the *steatite*, or soapstone; the *meerschaum*, of which pipe-bowls are cut; *olivine* and *serpentine*, which exist abundantly in the green marble of Galway: these are simple silicates of magnesia; others, as *amphibole* and *pyroxene*, are double silicates of magnesia and lime, more or less replaced by protoxide of iron.

Salts of Aluminum.

Chloride of Aluminum.—Al_2Cl_3. Eq. 1670·3 or 133·84. In a hydrated form this salt may be prepared by dissolving alumina in muriatic acid, a solution being obtained, which, when evaporated, yields very deliquescent crystals, containing twelve atoms of water. On applying heat to this, the salt itself is decomposed, muriatic acid is given off, and pure alumina remains. The dry chloride of aluminum is formed only by a process analogous to that described for chloride of silicon, p. 323. Pure alumina is mixed with lampblack and ignited in a porcelain tube, while a stream of dry chlorine is passed over it: the oxygen of the alumina combines with the carbon, and forms carbonic oxide, and the chlorine combines with the aluminum. The resulting chloride, being volatile, sublimes, and is condensed in the cool portion of the tube, which is allowed to project some distance beyond the furnace for that purpose, or a wide glass tube is adapted to receive the salt.

The chloride of aluminum thus formed is a pale-green crystalline mass. Exposed to the air, it fumes and deliquesces. Once combined with water, it cannot be freed from it. It is used to obtain metallic aluminum, as described p. 349.

The *Fluoride of Aluminum* is found in the mineral kingdom. The beautiful gem, the *topaz*, is a double fluoride and silicate of alumina.

Sulphate of Alumina $(Al_2O_3 + 3S.O_3) + 18$ Aq.—This salt is obtained by dissolving alumina in dilute sulphuric acid; it has a sweetish styptic taste, is very soluble in water, and crystallizes in thin flexible plates; when heated, it abandons its water, and at a red heat its sulphuric acid, alumina remaining pure. The sulphuric acid unites with alumina in many other proportions, of which that constituting the mineral *aluminite* is the most important; its formula is $Al_2O_3 + S.O_3 + 3$ Aq., the base, acid, and water each containing the same quantity of oxygen. This salt is produced, also, by adding an excess of caustic ammonia to a solution of alum; hence caustic ammonia cannot be used to prepare pure alumina (p. 351).

The sulphate of alumina combines with the alkaline sulphates to form the remarkable double salts, the common *alums*. The most ordinary kind is the *double sulphate of alumina and potash*, the formula of which is $(K.O.\,.\,S.O_3 + Al_2O_3 + 3S.O_3) + 24$ Aq.

From the large quantities of this salt employed in the processes of dyeing, its manufacture is conducted upon the great scale. In the coal districts, and underlying the beds of good coal, strata of clay-slate are generally found, containing a certain quantity of coally material, and through which abundance of bisulphuret of iron is disseminated in the instable rhombic form (see p. 332 and 358). When this *alum slate* is exposed to the air, the sulphuret of iron rapidly absorbs oxygen and forms copperas, with an excess of sulphuric acid, which reacts on the clays, with the alumina of which it combines. This effect is accelerated by the application of heat, which is applied by building up the mineral into pyramidal heaps, with some fuel underneath, and channels through the interior, by which a draught may be established; the fuel below being set on fire, the slate contains coal enough to maintain its own combustion, and the mass changes in colour as it burns, becoming brick red; according as the process is carried through, successive quantities of mineral are added to the burning heap, until it often acquires a height of sixty or eighty feet. When the mass thus calcined has become quite cold, it is powdered and lixiviated with water; a large quantity of sulphate of alumina and sulphate of iron dissolve out, and the liquor is brought by evaporation to a certain degree of strength. A solution of some salt of potash is then added, generally the waste chloride of potassium from soap-boilers, and the sulphate of iron being decomposed, forms sulphate of potash, which unites with the sulphate of alumina, and crystallizes out as alum, while the iron remains as chloride in the liquor.

In some volcanic countries, as Italy, a mineral is found already containing potash and sulphuric acid united to alumina, from which is obtained a very pure alum, *rock-alum*, which is valued very much by dyers, on account of its total freedom from sulphate of iron, of which English alum generally contains a small trace, which injures the colours of the dyes.

Alum crystallizes in regular octohedrons, the solid angles being often replaced by the surfaces of a cube. When heated, the water is first expelled, and at a red heat it parts with most of its sulphuric acid, sulphate of potash and pure alumina remaining. The taste of alum is sweet and astringent; it reacts acid, and is soluble in 18·4 parts of cold, and in 0·75 parts of boiling water. A remarkable pyrophorus, that of *Homberg*, is prepared from alum; three parts of dried alum and one of lampblack well mixed are to be placed in a stout glass bottle, and, being bedded with sand in a crucible, are to be carefully heated to redness, until a blue flame appears at the mouth of the bottle; when this has lasted a few minutes, the bottle is to be stoppered with a bit of chalk, and the whole cautiously cooled. The bottle contains a black powder, a mixture of lampblack, alumina, and sulphuret of potassium, which last, being in a state of exceedingly minute division, takes fire when a little of the product is shaken out of the bottle, and emits considerable light.

Basic Alum. Cubical Alum.—$Al_2O_3\,.\,2S.O_3 + K.O.\,.\,S.O_3$. This

substance, which is preferred as a mordant to ordinary alum, is prepared by adding carbonate of potash to a solution of alum, as long as the precipitate which first forms is redissolved by agitation. It crystallizes in cubes which have no acid reaction.

The sulphate of soda combining with sulphate of alumina, forms the *soda alum*, which is not much used. The ammonia alum will be hereafter noticed.

The *Phosphate of Alumina* constitutes a remarkable mineral found in Cork and Tipperary, the *wavellite*.

The simple and double silicates of alumina constitute probably the majority of all known minerals; such of them as possess technical or pharmaceutic value are noticed under the heads of the uses to which they are applied. For a description of the others, I refer to the ordinary works on mineralogy.

One substance, however, of which the constitution is very curious, may, from its technical importance, here be noticed, the *lapis-lazuli, ultramarine*. It is found in veins in igneous rocks in Siberia, but particularly in China. It is of a rich blue colour, not crystalline, and being powdered, serves in painting as the richest and most permanent blue; its composition has been found to be, in 100 parts, silica, 35·8; alumina, 34·8; soda, 23·2; sulphur, 3·1; carbonate of lime, 3·1: it is difficult to deduce a formula from these numbers, and the state of combination of the sulphur is not well understood. Attempts at imitating the composition of this body have been partially successful, and a large quantity of *artificial ultramarine* is now made for painters' use by the following process: freshly precipitated silicic acid and alumina are mixed with sulphur in a solution of caustic soda, all in the proportions above given, and the mixture dried down; the resulting mass is placed in a covered crucible and exposed to a white heat; it gives a dark and pure blue mass, to which, for the perfect bringing out of the colour, the air must have had partial access during its ignition. The product is reduced to impalpable powder by the same process adopted for the native substance.

Constitution of Glass and Porcelain.

I deferred the description of the silicates of potash, soda, and lime, because they stand so closely allied with the silicate of alumina, in relation to the important manufactures of glass and earthenware, that their properties could only be well understood when studied in connexion with it.

Silicic acid combines with the alkalies in many proportions, of which those that contain a considerable excess of base are soluble in water. Thus is prepared the *liquor of flints*, by melting together one part of powdered quartz and two of carbonate of potash; the carbonic acid is expelled, and a glassy mass is obtained, which deliquesces in the air, and is very soluble in water. It reacts strongly alkaline, and gives, with acids, a precipitate of silica in its soluble form, as described p. 321. In this preparation, soda may be substituted for potash in a proportion one third less, and a mixture of seventy parts of carbonate of potash, fifty-four of dry carbonate of soda, and 152 of fine quartz sand, gives a still more fusible and soluble product. This substance, under the name of *soluble* glass, has been employed to render wood incombustible, several coats of a strong solution of it being applied under the paint.

When the quantity of silicic acid is greater, the resulting alkaline silicate is insoluble in water, and possesses the qualities which give to glass its peculiar value. These are, first, to solidify, after being melted, very gradually, and to pass through a condition of pastiness, which admits of its being blown out, cut, and fashioned in every way; and, second, to remain, when solid, quite transparent, and destitute of any tendency to crystalline structure. Its composition

should also be such as to resist completely the action of air and water.

The materials used in the manufacture of glass are, 1st, quartz sand, as free as possible from iron; 2d, lime, used sometimes pure, sometimes slacked; occasionally chalk is employed in place of lime; 3d, carbonate of potash (pearl ashes of commerce); 4th, carbonate of soda, or a salt of soda, as Glauber's salt or common salt; 5th, old broken glass, technically termed *cullet;* 6th, red lead, which must be extremely pure; and for corrective purposes, arsenious acid sometimes, but more frequently black oxide of manganese.

These materials are by no means all employed together; the composition of various kinds of glass differing very much, as is shown in the following table of the best analyses of glass.

Constituents.	Hard white Glass.		Crown Glass.		Bottle Glass.		Crystal.	Flint Glass.	
	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.	No. 8.	No. 9.
Silicic Acid . . .	71·7	69·2	62·8	69·2	60·4	53·5	59·2	51·9	42·5
Potash	12·7	15·8	22·1	8·0	3·2	5·5	9·0	13·8	11·7
Soda	2·5	3·0	..	3·0	..	..	..	..	..
Lime	10·3	7·6	12·5	13·0	20·7	29·2	..	..	0·5
Alumina	0·4	1·2		3·6	10·4	6·0	..	..	1·8
Magnesia	..	2·0	2·6	0·6	0·6	..	..	..	..
Oxide of Iron . . .	0·3	0·5		1·6	3·8	5·8	0·4	..	..
Oxide of Manganese	0·2	..	..	..	..	..	1·0	..	..
Oxide of Lead . .	..	..	..	..	..	..	28·2	33·3	43·5
	98·1	99·3	100·0	99·0	99·1	100·0	97·8	99·0	100·0

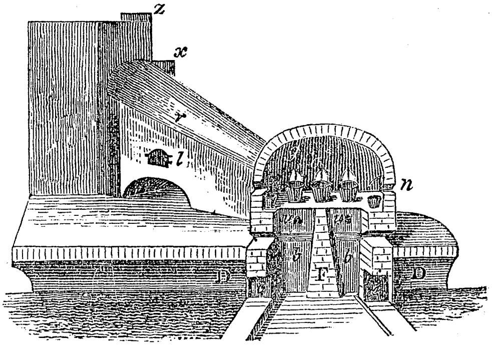
Although in some of these analyses a slight loss occurred, yet they are sufficiently accurate for all purposes. No. 1 is the hard Bohemian glass, so valuable to the chemist, from the high temperature it bears without softening. No. 2, also a Bohemian glass, is much more fusible, and is that in ordinary use. No. 3 is English plate, and No. 4 German plate glass. Nos. 5 and 6 are both French. Nos. 7 and 8 are English glass for table use and chemical apparatus; and No. 9 is the glass so celebrated for optical purposes, made by Guinaud.

It is difficult to trace any definite relation between the acid and bases in these glasses; indeed, we cannot look upon the different silicates as being really combined with each other; they are rather in a state of intimate mechanical mixture; hence, if the glass be kept soft, but not liquid, for a considerable time, the silicates gradually separate; the less fusible crystallizing, and rendering the glass opaque white. This takes place most easily with such glass as contains much silicate of lime or alumina. In this form, the mass is so hard as to strike fire with steel, and becomes almost infusible. From the name of its discoverer, it is termed *Reaumur's Porcelain.*

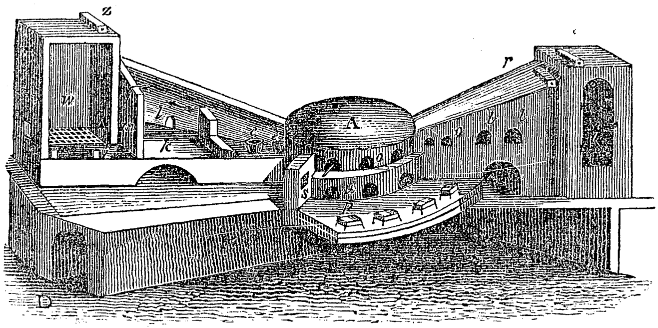
The arrangement of the furnaces for the manufacture of glass varies according to the materials and the kind of product. The materials, reduced to the state of very fine powder, are intimately mixed, and fused in crucibles of very refractory clay. The silica decomposes the carbonates of lime and potash or soda, and, expelling the carbonic acid, combines with the alkali and earth. If sulphate of soda had been used, a certain quantity of carbon is added, by which the sulphuric acid is decomposed, sulphurous and carbonic acids being evolved (p. 292), otherwise the silica could not completely expel the sulphuric acid. From the presence of minute quantities of protoxide of iron in the materials, the glass has, at first, a pale-greenish tint, which is counteracted by the addition of a little nitre or arsenious acid, these agents giving oxygen to the iron, which does not colour when peroxidized; with the latter body the metallic arsenic is evolved in vapour, the bad effects of which should prevent its employment. More generally peroxide of manganese is used, which, acting on protoxide of iron, produces peroxide of iron and protoxide of manganese, neither of which bodies gives any sensible tint to glass. If there be too much manganese employed, the glass acquires a violet tint. There is reason to suspect that soda glass is greenish even when absolutely free from iron.

The general arrangement of a glass furnace may be illustrated by reference to the figures, which represent the essential parts of one of the most perfect forms employed in the manufacture of the fine crown glass of Germany. In the oval furnace A, which is covered by a dome, the crucibles are arranged in two rows, on banks,

of which one is represented in the sectional figure. These crucibles are left open; but if employed for a glass containing lead, they should be covered by a hood, presenting only an aperture external to the furnace for the workman, as the glass would require to be thus protected from the smoke and combustible gases of the furnace, which would reduce the lead to the metallic state. Between the banks is a rectangular space for the fire, resting on the gratings *b b*, which are separated by the partition wall F, and have apertures at the sides for the introduction of the fuel. By



means of the passage D, there is access beneath the grate for the purpose of clearing it, and the draught is regulated by the opening or closing of the doors *e c*. The flame of the fuel, which should be either wood or a very bituminous coal, issues partly through the apertures in front of the crucibles *o o*, and partly passes by *g* into the wings and chimney; by means of the wings, a great quantity of the heat is economized for preparatory operations. Next the furnace are placed the fresh cru-



cibles *e e*, which, being always made in the glass-house, are there dried, baked, and ultimately brought to a full red heat, so as to be fit for introduction into the furnace with a charge of glass. The draught passing in the direction of the arrows over the low partition, the flame and hot air acts on the space *k*, on the floor of which are spread the materials for the next charge of glass, well mixed, and introduced by the apertures *l l;* these being brought to a dull red heat, undergo a commencement of vitrefaction, and are thus *fritted*, or prepared for the perfect combination by fusion in the crucibles. This operation of *fritting* was formerly performed in a separate reverberatory furnace. The draught escapes partly from the small chimney *x;* but a portion of the hot air, having passed over the partition *m*, is conducted into the chamber *w*, which is filled with wood supported on the grating; the hot air, in passing off, carries away the moisture of the wood, which is thus brought to a state of perfect desiccation, so as to give the greatest possible effect in the furnace.

For the perfect combination of the materials, and obtaining a mass free from streaks and air-bubbles, it is essential that the glass should be brought into a state of perfect liquidity, so as to allow the gases to pass off freely, and then be suffered to cool until it acquires the pasty consistence which fits it for being worked into the necessary forms. In thus cooling down, however, those glasses which contain oxide of lead frequently separate into two or more layers of glass of different densities, which, when stirred up by the tools of the workman, give by their imperfect mixture a clouded and streaked appearance to the articles made from such glass. This impefection is peculiarly fatal to glass for optical purposes, as each layer may have a different refractive power, and thus give distorted images.

The great use of glass in the arts and in ordinary life depends upon its plasticity at a red heat, which renders it capable of being moulded into every form; its insol-

ubility in water; its resisting the action of acids and the generality of chemical reagents under all ordinary circumstances; its transparency and lustre, and the relations to heat, to light, and to electricity, which have been already fully noticed. From the low conducting power of glass for heat, thick portions of it are liable to break when suddenly warmed, the part to which the heat is directly applied expanding, and thereby separating from that which remains cold. When a lump of glass is suddenly cooled, as by being laid, while soft, on a plate of cold iron, or being dropped into water, the internal portions being prevented from contracting, remain in a state of instable arrangement, on which depends its double refracting and polarizing properties (p. 230). When the molecules of such a piece of chilled glass are made to vibrate, by being scratched, or a little fragment being broken off, they change totally their disposition, and, flying asunder, the mass crumbles into powder with an explosion. *Prince Rupert's drops*, with which this property of glass may be exemplified, are prepared by taking up on an iron rod a little melted glass, and allowing the drops of it to fall into a vessel of cold water; when one is held in the hand, and the long projecting tail broken off, a smart blow is felt with a dull noise, and the drop is found to be reduced to fine powder. As this excessive frangibility would render glass unfit for most household and chemical purposes, it is necessary to lessen it as much as possible, which is done by allowing it to cool very slowly. For this purpose, the vessels, when formed, are placed in the *annealing furnace*, or *leer*, which is a long gallery containing a number of iron trays moveable along it by means of an endless chain; the hot glass articles are placed in the trays at one end, where a strong fire is made, the flame of which sweeps to a certain distance into the gallery. According as new trays come up, those already full are drawn down into the cooler part of the gallery by the chain, and finally issue at the other end quite cold. The passage down occupying from twenty-four to forty-eight hours, the particles of the glass, in cooling, have time to assume their most stable arrangement, and may then be exposed, if not very thick, to changes of temperature, provided they be not very sudden.

The specific gravity of glass varies with its composition from 2·4 to 3·6, the latter being that of flint glass, containing 40 per cent. of oxide of lead. The lighter glasses are generally those which are hardest, and resist the action of water and of reagents best. The oxide of lead in flint glass is acted on by a variety of chemical substances, which unfits it for many laboratory uses. Where alkali predominates, the glass is rapidly acted on by the air, attracting moisture, and thus frequently embarrassing electrical experiments. Bottle glass which contains much alumina is so rapidly corroded by the cream of tartar in wine, as sometimes to become opaque, and spoil the wine in the course of a few days.

I have had frequent occasion to notice the various coloured glasses produced by the addition of metallic oxides (see p. 37); on this principle is founded the art of painting on, or staining glass, and also the manufacture of artificial gems. These arts I shall have to notice farther on, and any detail of their methods would be foreign to a work like the present.

The manufacture of porcelain and earthenware depends on two principles, first, that of the plasticity and fusibility of clay, and, secondly, the fusibility of a glass by which the substance of the porous clay may be imbibed, and thus rendered water-tight. Clay, when perfectly pure, is a neutral silicate of alumina, $Al_2O_3+3Si.O_3$; but as the great deposites of clay used for the purposes of the arts are produced by the weathering (decomposition) of a variety of rocks, a number of foreign ingredients are intermixed in small quantity, and produce varieties which influence very much the proportions used in the manufacture. The purest porcelain clay is formed by the decomposition of the feldspar contained in granitic and syenitic rocks. The feldspar has the formula $K.O..Si.O_3+(Al_2O_3+3Si.O_3)$ by the action of water, the silicate of potash is dissolved out as soluble glass (p. 437), and the silicate of alumina remains as a fine

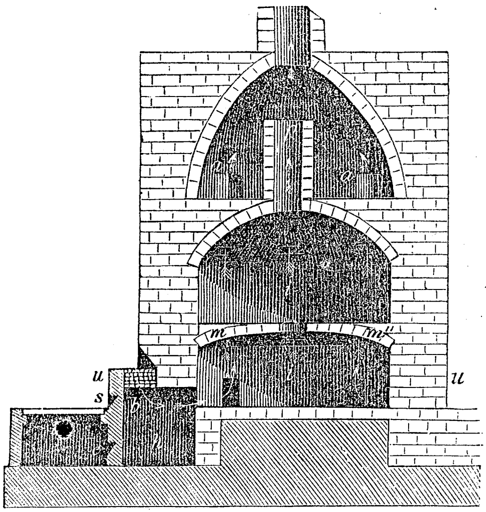
powder, perfectly white, impalpable, forming with water a paste capable of being moulded into any form, and, when heated, abandoning the water and contracting in volume, but retaining the form which had been given to it. The pure porcelain clay is seldom found, and hence is used only for the finest objects; other clays of greater or less purity are therefore used, either alone, or mixed with porcelain clay, for such objects as stone-china and delft; and clays in which a quantity of alumina is replaced by iron, and which, consequently, when burned, assume a red or yellow colour, are employed for common earthenware. In the clays which contain very little iron, and hence burn white, there are present, almost universally, certain quantities of alkali, remaining from the decomposed feldspar; this is generally potash, but may be soda when the clay is formed from albite ($Na.O..Si.O + 3Al_2O_3 + 3Si.O_3$); and when the source of the clay is not a pure granitic rock, the associated minerals generally yield a certain quantity of lime which mixes with it. Hence the composition of the following clays, from various countries, used in the manufacture of porcelain, can easily be accounted for:

Clay from	Morl.	Schneeberg.	Limoges.
Silica	71·42	43·6	46·8
Alumina . . .	26·07	37·7	37·3
Lime	0·13	. . .	. . .
Potash	0·45	. . .	2·5
Water	. . .	12·0	13·0
Oxide of Iron . .	1·93	1·5	. . .

If clay alone were used in the fabrication of earthenware, although, from its plasticity, it would assume perfectly the required form, yet, from its infusibility, it would, when baked, have so little coherence, and, from its great contraction, be so liable to crack, that in practice it could not be beneficially employed. The paste of which the china and delft articles are made, consists, therefore, of clay, to which is added silica, lime, and potash—in other words, the constituents of crown glass—which, being fusible at a high temperature, cement together the particles of clay, and enable the different portions of the vessel to hold together during the bakings. Thus, to form the body of ironstone chinaware, forty parts of Devonshire clay are mixed with from forty to sixty of feldspar, and generally about five parts of flint glass and ten of quartz.

It would not be within the object of the present work to detail the mechanical process of fashioning articles of earthenware. When formed, they are first dried in the air, and then heated moderately, to expel as much water as will fit them for the reception of the *glaze*. This consists in covering them perfectly with a sheet of easily-fusible glass, which, by entering into all their pores, and varnishing their surface, renders the vessels impervious to water; the glassy constituents of the paste having, in quantity and fusibility, only sufficient power to cement the particles of the clay together, without depriving the mass of its porosity. The composition of the glaze may vary much in different establishments; an ordinary one, for ironstone china, consists of feldspar 36, quartz 20, white lead 40, flint glass 8. These materials are fritted together, and then, being reduced to impalpable powder, are diffused through water, into which the vessel to be glazed is dipped, and is then taken out again. The clayey substance of the vessel rapidly imbibes the water, and the fine powder of the glaze remains uniformly spread upon the surface. The articles so prepared are arranged in capsules of a very refractory ware, and placed in the kiln or furnace to be baked. The construction of the porcelain kiln is represented in the figure. It is a

vaulted building, generally of three stories, provided with five fireplaces, from which



the flames pass into the kiln by the passages *b*, *m*, *a*, *p*, marked with the arrows; from the third story the chimney issues. The highest floor is reserved for drying the capsules in which the articles to be baked are arranged; on the floor of the second, the articles are dried to the degree which fits them for the reception of the glaze; and in the lowest chamber, by the full action of the fire, the final baking is performed. The operation commences, first, with a moderate fire, the fuel being introduced into the cavity *h*, and supplied with air by the apertures *e s;* the heat being allowed to rise gradually for six or eight hours, the space becomes full of ignited fuel, and a strong draught is established. The apertures are then closed, fuel (and for this, as for glass-making, wood answers best) is heaped on the rest *b*, and the air admitted to the kiln only after having passed through *h*. The temperature is thus kept uniformly intense for seventeen or eighteen hours, and then, the kiln being allowed to cool slowly for three or four days, the articles are extracted in their finished state.

The glaze on earthenware being a transparent glass, it may be coloured by various metallic oxides, and thus the patterns produced which give to the finer kinds of ware so much popularity. The coloured glass, being reduced to fine powder, is mixed up with oil of spike, and either laid on with a brush, as in ordinary painting, or printed, in a very ingenious manner, by having the pattern engraved on copper, and printing it with the glaze made with oil into a very thin ink on damp tissue paper. The paper with the figure thus formed is laid evenly on the vessel, which, from its porosity, immediately absorbs the liquid materials of the ink, and leaves the powder of the glaze on the surface in all the fine tracings of the design. The paper is then cautiously rubbed off by the finger in a vessel of cold water, and the uniform glazing applied over all, as before described. The blue patterns are produced by cobalt; the black by a mixture of oxides of iron and manganese; the crimson by gold; and gold and platina are applied also in their metallic state, by dissolving their chlorides in oil of turpentine, and applying this varnish with a pencil, then burning, and burnishing the metallic surface.

A coarse kind of glazing, given to the common articles of earthenware, is produced by throwing into the kiln, when intensely hot, a few handfuls of common salt; by means of the watery vapour produced by the combustion of the fuel, the silicic acid on the surface of the earthenware decomposes the common salt, which is converted into vapour by the heat; $Si.O_3$ with $Na.Cl.$ and $H.O.$, producing $Na.O. . Si.O_3$, which forms a transparent glassy varnish on their surface, while $H.Cl.$ passes off with the excess of watery vapour, forming copious white fumes.

The general characters of the salts of *glucinum*, *thorium*, *yttrium*, *zirconium*, *lanthanum*, and *cerium* have been noticed under the heads of these respective metals (p. 351, *et seq.*), and do not require farther detail.

Salts of Manganese.

Manganese may give origin to four classes of salts, in two of which it constitutes the base, and in the others forms an element of the acid; these last, the *manganates* and *permanganates*, have been noticed in p. 356, and it remains only to describe the former.

Protochloride of Manganese.—Mn.Cl. + 4 Aq. Eq. 788·5 + 450 or 63·19 + 36. This salt may be obtained by digesting the commercial black oxide in muriatic acid until all the excess of chlorine has been expelled, then evaporating to dryness, and fusing the mass, at a bright red heat, in a crucible. The chloride of iron, which is formed by the impurities of the ore, is decomposed by the last portions of water, and muriatic acid being given off, oxide of iron remains. Hence, on digesting the melted mass in water, protochloride of manganese dissolves, and all the iron remains insoluble. The solution, which is of a pale pinkish tint, is to be evaporated, and the salt crystallized. The crystals are rhombic tables, rose coloured; by heat they lose their water of crystallization, but are not otherwise altered. It is known to be free from iron when its solution gives, with yellow prussiate of potash, a pure white precipitate.

Perchloride of Manganese, $Mn.Cl_2$, appears to be formed when strong muriatic acid is digested on peroxide of manganese without heat. A gentle heat resolves it into protochloride and free chlorine.

Protosulphate of Manganese.—$Mn.O..S.O_3 + 7$ Aq. This salt may be obtained pure from the commercial oxide by mixing this into a thick cream with oil of vitriol, and heating it in a shallow dish until it becomes quite dry, oxygen being given off. The dry mass which contains the mixed sulphates of iron and manganese is to be then placed in a crucible, and heated to bright redness; the sulphate of iron is decomposed, its sulphuric acid being expelled by the heat; but the sulphate of manganese is not altered, and on digesting the resulting mass in water, dissolves, and is obtained crystallized by evaporation and cooling. This salt crystallizes in oblique rhombic prisms with 7 Aq., but is also found with 5 Aq. and with 4 Aq., its form changing in each case. In all, one equivalent of water is constitutional, and may be replaced by an alkaline sulphate, with which the sulphate of manganese forms double salts, like those of sulphate of magnesia.

Sesquisulphate of Manganese, $Mn_2O_3 + 3S.O_3$ may be obtained by dissolving the sesquioxide in sulphuric acid. The solution is of a rich crimson colour: when heated, it becomes colourless, giving off oxygen, and it is instantly bleached by sulphurous acid or any deoxidizing agent. Its most important property is that of forming with the sulphate of potash or of ammonia double salts, crystallizing in octohedrons, which are *manganese alums*, similar in constitution to the ordinary alum, but with Al_2O_3 replaced by Mn_2O_3.

No other salt of manganese requires special notice.

Salts of Iron.

There are two series of iron salts, corresponding to the two oxides, *proto-salts* and *sesqui-salts.*

Protochloride of Iron.—Fe.Cl.+4H.O. This salt is formed when metallic iron is dissolved in muriatic acid, hydrogen being evolved; the solution, which is of a pale bluish-green colour, yields, on evaporation, rhombic crystals of the hydrated chloride, which are slightly deliquescent. This solution absorbs oxygen from the air with great avidity, and becomes dark-green coloured. When these crystals are heated they lose water, and, if the air have not access, a white mass of dry protochloride of iron is obtained, but otherwise perchloride is formed and the whole decomposed. The anhydrous protochloride is very elegantly prepared by passing a stream of dry chloride of hydrogen over fine iron wire, coiled up in a tube of hard Bohemian glass, and heated to bright redness: hydrogen gas is evolved, and protochloride of iron formed, which sublimes into the cold part of the tube as brilliant white spangles. By the action of the air it is rapidly decomposed.

Sesquichloride of Iron.—Fe_2Cl_3. This salt is formed when iron is dissolved in aqua regia; a deep brown solution is obtained, which, when evaporated to the consistence of a sirup, gives large red crystals of hydrated chloride, which are very deliquescent. On the application of heat, this salt is totally decomposed; muriatic acid is given off, and the red oxide of iron remains behind, with some unaltered chloride, as a basic salt. To obtain the anhydrous sesquichloride, a stream of dry chlorine gas is to be passed over iron wire heated to redness in a tube of Bohemian glass. The iron burns in the chlorine, and the salt sublimes into the cool portion of the tube, where it forms a dark olive crystalline mass, which rapidly attracts moisture from the air. This salt is very soluble in alcohol.

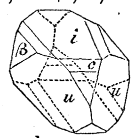
The sesquichloride of iron, when dissolved along with sal ammoniac, may form a true double salt, containing an equivalent of each salt; but the crystals which are generally thus obtained, although deeply-coloured red, contain but two or three per cent. of the chloride of iron.

Protoiodide of Iron, Fe.I., is formed by digesting iodine in water on an excess of iron filings. Considerable heat is evolved, and a colourless solution is obtained, which, when evaporated, yields a crystalline mass containing water of crystallization, and which is decomposed by a farther action of the heat, iodine being evolved. It absorbs oxygen very rapidly. A solution of protoiodide of iron dissolves iodine abundantly, becoming brown, and possibly containing the sesqui-iodide, Fe_2I_3; but it is more likely that the iodine is not combined, as it is sensible to the test of starch.

The *bromides of Iron* resemble perfectly the iodides.

Protosulphate of Iron. Green Copperas.—Fe.O..$S.O_3$+7 Aq. The manufacture of this salt is conducted on the large scale for the purposes of the arts, by exposing to the action of air and moisture the nodules of bisulphuret of iron, which are found abundantly in the strata of alum-slate-clay (p. 436). Oxygen is rapidly absorbed both by the iron and the sulphur, sulphuric acid and oxide of iron being

formed, and the liquor which, holding these in solution, drains from the beds of decomposing pyrites, is run into tanks, where it is put in contact with pieces of old iron, which serve to neutralize the excess of acid produced from the pyrites, being a bisulphuret, and also, by means of the hydrogen evolved, to retain all the iron in the state of protoxide; after proper evaporation, the salt is obtained crystallized from these solutions. On the small scale, it may be prepared by dissolving iron wire in dilute sulphuric acid, as in the process for preparing hydrogen gas (page 247). The protosulphate of iron generally crystallizes with seven atoms of water, of which one is constitutional, and may be replaced by an alkaline sulphate, forming double salts. The form of its crystal is a short oblique rhombic prism, *i*, *u*, *u*, with numerous secondary faces, as β, *c*, in the fig. Its taste is styptic and metallic; it dissolves in 1·64 parts of water at 50°, and in 0·30 parts at 212°. Like the other protosalts of iron, it is but very sparingly soluble in alcohol. When heated, it abandons first its water, and at full red heat its sulphuric acid,



of which a portion is decomposed into sulphurous acid and oxygen, by which the iron becomes peroxidized. The peroxide of iron thus formed is used in the arts, under the names of *rouge* and *colcothar*, as a polishing material. On these properties is founded the manufacture of fuming oil of vitriol, described in page 247. The protosulphate of iron absorbs oxygen rapidly even when dry, and becomes covered with a reddish crust of basic persulphate, whence its commercial name. In solution, the absorption of oxygen proceeds quickly, until two thirds of the iron are peroxidized and a reddish solution obtained, from which alkalies throw down the black magnetic oxide (see page 363). This solution does not crystallize.

Sesquisulphate of Iron.—$Fe_2O_3+3S.O_3$. Eq. 2481·9 or 198·9. This salt is found native in large quantities in Chili, combined with 9 Aq. It may be prepared artificially by pouring oil of vitriol on red oxide of iron, stirring the mass well, and applying a moderate heat to expel the excess of acid. The salt may then be dissolved in water, forming a red solution, and giving, when evaporated, a deliquescent mass scarcely crystallized. In this way it retains an excess of acid, which may be driven off by a heat just below redness. The persulphate then appears as a white powder, which dissolves but very slowly in water. By a strong heat this salt is totally decomposed. The protosulphate may be converted into persulphate by adding to a boiling solution nitric acid in small quantities, as long as any nitric oxide gas is given off. There are several basic persulphates of iron, of which the most important is the rust-coloured powder, which precipitates from a solution of protosulphate of iron when oxidized by exposure to the air; its formula is $2Fe_2O_3+S.O_3+3$ Aq.

The persulphate of iron combines with the alkaline sulphates to form a class of *alums*, which contain Fe_2O_3 in place of Al_2O_3. These iron alums are generally pale red in colour, but have the form, solubility, and nearly the taste of common alum.

Protonitrate of Iron may be formed by dissolving sulphuret of iron in cold dilute nitric acid; it crystallizes in pale-green rhombs, which, when heated, evolve nitric oxide gas, and form a basic ni-

trate of the peroxide. Metallic iron dissolves in dilute nitric acid without the evolution of any gas, water and nitric acid being simultaneously decomposed, and oxide of iron and ammonia produced. Thus $N.O_5$ with $3H.O.$ and $6Fe.$, give $6Fe.O.$ and $N.H_3$.

Pernitrate of Iron is produced when iron is dissolved in hot nitric acid; the solution is reddish brown, and gives, by drying, a deliquescent mass easily decomposed by heat. When a solution of this salt is decomposed by carbonate of potash added in excess, the oxide of iron, which first precipitates, is redissolved, and a deep red liquor obtained, which is sometimes used in medicine under the name of *Stahl's alkaline tincture of Iron.*

Protophosphate of Iron, Tribasic—$H.O. . 2Fe.O.+P.O_5$—may be formed by decomposing a solution of protosulphate of iron with tribasic phosphate of soda. It is a white powder, which rapidly becomes blue by exposure to the air, a portion of the iron becoming peroxidized. This blue phosphate of iron is a double salt, which exists in nature, forming the *bog iron ore*, and may be produced artificially by adding solution of phosphate of soda to the solution of mixed sulphate of iron, from which alkalies precipitate the black oxide (p. 363). The precipitate which forms is of a rich blue colour, and is not changed by exposure to the air. Its formula is $(H.O..2Fe.O.+P.O_5)+(2Fe_2O_3.P.O_5)$. It is used in medicine.

Sesquiphosphate of Iron, $2Fe_2O_3+P.O_5$, is obtained by decomposing a solution of sesquisulphate of iron by phosphate of soda. It is a white powder, insoluble in water. It is used in medicine.

The salts of the protoxide of iron are remarkable for absorbing nitric oxide in considerable quantity, and forming therewith a deep olive-coloured liquor, which rapidly attracts oxygen from the air. The quantity of gas absorbed is one atom for two atoms of salt, and the nitric oxide may be considered as replacing the third atom of oxygen, which forms the sesquioxide. Thus the protochloride gives $Fe_2+Cl_2.N.O_2$, and the protosulphate $(Fe_2+O_2.N.O_2)+2S.O_3$, analogous to $Fe_2+Cl._3$ and $(Fe_2+O_3)+2S.O_3$. The utility of this olive liquor as a test for nitric acid and in eudiometry, has been noticed in p. 264 and 281.

Salts of Nickel and Cobalt.

Chloride of Nickel, Ni.Cl., may be obtained by dissolving oxide of nickel in dilute muriatic acid, or by acting on the metal with the hot concentrated acid. It crystallizes in emerald green rhombs. When heated, it loses its water of crystallization, and gives a yellow powder, which by a red heat sublimes in crystals, resembling *Mosaic gold.*

Sulphate of Nickel.—$Ni.O..S.O_3$. This salt is obtained by dissolving the oxide in dilute sulphuric acid, or by acting on the metal with a mixture of nitric and sulphuric acids diluted with water; the nitric acid then supplies oxygen. This solution gives fine emerald green crystals, which vary in form according to the quantity of water they contain. When they form below 60°, they are long rhombic prisms, containing 7 Aq., and isomorphous with the sulphates of zinc and magnesia; but when formed at any temperature above 60°, the quantity of water is six atoms, and the form is an octohedron with a square base. If a prismatic crystal be exposed to a moderate heat or to sunshine, it gives off an atom of water, and becomes oqaque by breaking up into a number of very minute crystals of the octohedral form. In sulphate of nickel one atom of water being constitutional, may be replaced by the alkaline sulphates, and double salts formed, of which some are very beautiful.

Chloride of Cobalt, Co.Cl., is formed by dissolving oxide of cobalt, or the *zaffre* of commerce, in muriatic acid. The solution is

pinkish, and gives, on evaporation, rose-red crystals of hydrated chloride; if the evaporation be pushed very far, the liquor becomes blue, and dark blue crystals of anhydrous chloride are deposited. If the solution contains nickel, which is always the case when prepared from zaffre, the colour becomes green, and it is thus that sympathetic inks of cobalt are produced, and summer and winter scenes in landscapes alternated; the surface of a drawing washed with a very dilute solution of chloride of cobalt being white until dried before the fire, but then becoming grass green.

Sulphate of Cobalt, $Co.O.+S.O_3$, is obtained by treating zaffre with sulphuric acid. In its general characters it resembles the chloride; when heated strongly, it gives off sulphuric acid, and oxide of cobalt remains; it contains six atoms of water of crystallization, and gives a double salt with sulphate of potash.

Phosphate of Cobalt, $H.O..2Co.O.+P.O_5$, is precipitated in dark violet flocks when solution of sulphate of cobalt and phosphate of soda are mixed together. This substance is the basis of a very beautiful pigment, *Thenard's Blue*, which is prepared by mixing intimately one part of phosphate of cobalt with two or three of alumina, and exposing the mixture to an intense white heat in a wind furnace. The blue tint thus given to alumina serves as a test for that earth, particularly to distinguish it from magnesia by the blowpipe. (See p. 349 and 351).

Silicate of Cobalt constitutes the blue smalts employed to tinge paper and to colour glass; the finest kind is known in commerce as *azure*. Its manufacture is conducted on the great scale in Saxony and Sweden, and is the process in which most of the arsenic of commerce is obtained, that being expelled in the roasting of the cobalt ores (p. 366, 376). From the zaffre a sulphate of cobalt is prepared, and on the other hand a silicate of potash, by melting together fine sand and carbonate of potash; these solutions being mixed, silicate of cobalt is precipitated, while sulphate of potash remains dissolved. This precipitate is the best material for colouring porcelain and glass; but the ordinary smalts are formed by melting impure carbonate of cobalt with potash and quartz into a blue glass, which is then reduced to impalpable powder, and sorted according to the quality, for commerce.

Salts of Zinc and Cadmium.

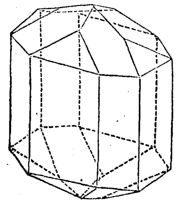
Chloride of Zinc—Zn.Cl.; Eq. 845·9 or 67·78—may be prepared by burning metallic zinc in chlorine, or by dissolving the metal in muriatic acid. The solution is colourless; when evaporated, it yields rhombic crystals, which contain water, and deliquesce with extreme rapidity. The dry salt is white, and melts a little above 212°, so that a solution, when evaporated, never becomes solid. It is hence sometimes applied as a bath in place of oil or fusible metal, in taking the specific gravity of vapours (p. 14). From its fusibility and softness, it had formerly the name of *Butter of Zinc*. From its affinity for water, it acts powerfully as a caustic on the living tissues, and is employed in medicine as such.

Chloride of zinc combines with oxide of zinc in many proportions, forming oxychlorides, of which there are three worthy of notice: the first, which is long known, is formed by decomposing chloride of zinc by a small quantity of ammonia; its formula is Zn.Cl.+3Zn.O.+4 Aq. The second results from the action of water on the ammoniacal chloride of zinc; its formula is Zn.Cl.+6Zn.O.+10 Aq., and is that whose analogies to the liquid muriatic acid have been pointed out in p. 309. The third is formed by acting on chloride of zinc with an excess of potash; its formula is Zn.Cl.+9Zn.O.+14 Aq.

The *bromide* and *iodide of Zinc* resemble completely the chloride in general characters: a solution of iodide of zinc is capable of dissolving a large quantity of iodine.

Sulphate of Zinc, $Zn.O.\,.\,S.O_3+7$ Aq., may be produced by dissolving the metal in dilute sulphuric acid. For the purposes of the arts, it is made upon the great scale by roasting, in a current of hot air in a reverberatory furnace, the native sulphuret of zinc, *blende*

The metal and sulphur both combining with oxygen, a neutral sulphate of the oxide is formed, which being then dissolved out by water, the solution is evaporated to a pellicle, and allowed to crystallize. Sometimes the blende, in place of being roasted, is exposed on sloping beds to the action of the air and moisture, when it gradually attracts oxygen, and is treated as has been described under the head of sulphate of iron. The crystals which first form are heated until they undergo watery fusion, and are then poured into conical moulds, where they solidify, and the salt is thus sent into commerce in masses like sugar-loaves: its commercial name is *white vitriol*. The crystals of sulphate of zinc are eight rhombic prisms, as in the figure, containing 43·9 per cent. of water, and are soluble in two and a half times their weight of cold water. It is permanent in the air. It combines with the alkaline sulphates, which replace its constitutional water, forming double salts, and with oxide of zinc to form basic salts, of which several are known, and which agree in constitution with the oxychlorides of zinc. Their composition has been already noticed in p. 368.



Nitrate of Zinc, $Zn.O..N.O_5$, is obtained by dissolving the metal in dilute nitric acid; it crystallizes in flat four-sided prisms. It is deliquescent, and soluble in alcohol.

No other salt of zinc is of importance.

Chloride of Cadmium, Cd.Cl., crystallizes in large four-sided prisms; it is not deliquescent. The other salts of cadmium resemble completely the corresponding salts of zinc, and do not require notice.

Salts of Tin.

Protochloride of Tin.—Sn.Cl. + 3 Aq. Eq. 1177·9 + 337·5 or 94·39 + 27. This salt is obtained anhydrous by heating tin in a current of muriatic acid gas, hydrogen being evolved; or by distilling a mixture of equal parts of tin and corrosive sublimate in a glass retort, the metallic mercury first passes over, and, finally, the protochloride of tin sublimes at a strong red heat. It forms a gray glassy mass. In combination with water, it may be obtained by dissolving tin in strong muriatic acid until it is saturated, and on evaporation the salt crystallizes in long prisms, which contain three atoms of water. When these crystals are heated, they first lose water, but afterward muriatic acid passes off, and a basic salt remains. This crystallized protochloride, under the name of *salt of tin*, is used extensively in dyeing as a mordant; in its preparation on a large scale, copper vessels may be employed, because, as long as any metallic tin is present, the copper is electrically protected by it, and is not acted on by the acid. This salt is very soluble in water, but is decomposed by a large quantity, a basic salt, Sn.Cl + Sn.O., being thrown down; hence, in order to have a dilute solution clear, it requires the addition of a few drops of muriatic acid. Protochloride of tin is remarkable for its affinity for oxygen and for chlorine; it reduces the salts of silver, quicksilver, and gold to the metallic state, and the salts of copper, iron, and manganese to the lowest state of oxidation. It acts similarly on many organic substances, as indigo, litmine, orceine; forming colourless compounds, which have some important applications in the art of dyeing.

The protochloride of tin combines with chloride of potassium and with sal ammoniac to form double salts, which were analyzed by Apjohn.

Perchloride of Tin, $Sn.Cl_2$, is prepared anhydrous by distilling a mixture of four parts of corrosive sublimate and one of metallic tin; at a very moderate heat, a colourless liquid distils over, which forms dense white fumes where it comes into contact with the air: this is the bichloride of tin, the *fuming liquor of Libavius*. Metallic mercury remains in the retort. This singular compound boils at 248° Fah.; the specific gravity of its vapour is 9·12. When mixed with one third of its weight of water, it solidifies into a crystalline mass, and it is hence that it forms such dense fumes by exposure to damp air. It may be prepared in this crystallized form by dissolving tin in nitromuriatic acid and evaporating the solution, or by passing chlorine into a solution of protochloride as long as it is absorbed. If the crystals be heated, they are decomposed, muriatic acid being given off, and peroxide of tin remaining.

Protoiodide of Tin, $Sn.I.$, may be formed by heating together tin and iodine, or by mixing solutions of iodide of potassium with a slight excess of protochloride of tin. It is a brownish red mass, soluble in water, and crystallizing from the solution in long prisms of a bright orange colour. It is decomposed by a large quantity of water. It combines with the iodide of potassium to form a soluble double iodide. The *biniodide* of tin crystallizes in yellow needles, which are decomposed by much water.

The *bromides of Tin* are not important.

Protosulphate of Tin, $Sn.O..S.O_3$, is formed when tin is dissolved in strong sulphuric acid. A saline mass is obtained, which dissolves in water, giving a brown solution, from which the salt crystallizes in small needles. *Bancroft's mordant*, for dyers, is prepared by digesting two parts of tin with three of strong muriatic acid for an hour, and then adding one and a half parts of oil of vitriol very cautiously. The mass becomes hot, and the tin is rapidly dissolved. The heat is to be kept up on the sand-bath as long as hydrogen is evolved. The solution, on cooling, forms a crystalline mass, which is to be dissolved in water, so that eight parts of the solution shall contain one of tin.

The sulphuric and nitric acids may be neutralized by freshly-precipitated peroxide of tin; but these salts possess very little stability, and are of no technical or scientific interest. The peroxide of tin itself acts as an acid, and its relations to the alkalies have been described in p. 371.

The sulphurets of tin act as sulphur acids, combining with the sulphurets of the alkaline metals. The *bisulphuret* forms with sulphuret of sodium a crystallizable salt, $2Na.S.+Sn.S_2+12$ Aq., *sulphostannate of Sodium.*

Salts of Chromium and Vanadium.

There are two kinds of salts of chrome, one in which the oxide of chrome is the base, and the other in which the chromic acid is combined with bases.

A. Salts of Oxide of Chrome.

Chloride of Chrome.—Cr_2Cl_3. Eq. 2031·6 or 162·8. When oxide of chrome is mixed with lampblack, and treated by a current of dry chlorine at a red heat, as described for the preparation of the chlorides of silicon and aluminum, the chloride is obtained sublimed in the cold part of the tube in peach-blossom-coloured scales of exceeding beauty. It may also be obtained by dissolving oxide of chrome in muriatic acid, and evaporating the solution; it remains as a green mass, in which it is combined with 3H.O. When heated to 450°, it froths up very much, gives off that water, and forms a rose-coloured mass not so beautiful as that obtained by the process first described.

Chlorochromic Acid.—$Cr.Cl_3+2Cr.O_3$. This singular compound is obtained by melting together in a crucible ten parts of common salt and seventeen of bichromate of potash; the melted mass is poured out on a slab, and broken into small pieces, with which a tubulated retort may be filled, and after a receiver and condensing apparatus have been attached, forty parts of oil of vitriol are to be poured on the mass. The decomposition occurs so violently, that in a few minutes all the product distils over, without the application of external heat. This substance is a thin bl od-red

liquid appearing black by reflected light; it fumes much by exposure to the air; its vapour is red like nitrous acid. When its vapour is heated to redness, it is decomposed, as described in p. 373. It is decomposed by water. Alcohol placed in contact with it takes fire, burning with a bright flame; phosphorus acts in the same way. This substance may either be looked upon as a compound of perchloride of chrome with chromic acid, $Cr.Cl_3+2Cr.O_3$, or as a compound of chlorine with a deutoxide of chrome, $Cr.O_2Cl$. The analogy of the sulphuric to the chromic acid is supposed to favour this latter view, as also the sp. gr. of its vapour, which is 5·9.

Sulphate of Chrome, $Cr_2O_3+3S.O_3$, may be formed by dissolving oxide of chrome in dilute sulphuric acid, but does not crystallize. Its only important character is, that it combines with the sulphates of potash or of ammonia to form double salts, the *chrome alums*, which crystallize in dark purple octohedrons, and which contain the same proportion of acid, alkali, and water as common alum, but oxide of chrome in place of alumina. The solution of chrome alum in cold water is purple, but when heated it becomes green, and the elements of the salt are then found to be no longer united, as by evaporation they may be separated. It would appear, indeed, that almost every salt of chrome may exist in either a green or a red condition, and that in the former they do not crystallize. The chrome alum is obtained abundantly by setting aside for a few days the residue of the process for making aldehyd, as described farther on.

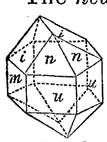
The *Perfluoride of Chrome*, $Cr.F_3$, is formed by acting with oil of vitriol on a mixture of powdered fluor spar and bichromate of potash in a platinum retort. It is a gas of a rich crimson colour, which can only be collected in a platinum crucible inverted in the quicksilver trough. Its decomposition by water, and the consequent formation of chromic acid, has been already noticed, p. 373.

B. *Salts of Chromic Acid.*

Chromates of Potash.—The manufacture of the bichromate of potash, $K.O.+2Cr.O_3$, is carried on extensively, as it is from that salt that all the compounds of the metal used in chemistry or in the arts are prepared. It is made from the only abundant ore of chrome, the *chrome-iron*, $Fe.O.+Cr_2O_3$, by the following process. Two parts of the ore, ground to a fine powder, are intimately mixed with one part of saltpetre, or four parts of ore are used with two parts of pearl ashes and one of saltpetre, and the mixture exposed for several hours on the floor of a reverberatory furnace to a violent heat. Under the influence of the potash, the oxide of chrome absorbs the oxygen from the air, and forms chromic acid. The calcined mass is lixiviated with water, and a deep yellow liquor is produced, which contains neutral chromate of potash, which may be obtained crystallized by evaporation; but as this salt is not well suited for the purposes of commerce, it is generally changed into the bichromate by adding to the liquor a quantity of sulphuric acid, which takes one half of the potash, and the bichromate is then obtained by crystallization in tanks lined with lead.

Bichromate of Potash crystallizes in large four-sided prisms and square tables of a rich orange-red colour. It melts easily, and in cooling crystallizes in another form. It is soluble in ten parts of cold water. It is not decomposed except by a white heat, which expels oxygen, and leaves a mixture of oxide of chrome and neutral chromate of potash.

The *neutral Chromate of Potash*, $K.O. \,.\, Cr.O_3$, may be prepared by adding to a solution of bichromate of potash as much more alkali as it already contained. It is soluble in twice its weight of cold water. Its solution is intense golden yellow; it crystallizes in rhombic prisms, isomorphous with those of sulphate of potash, as in the figure, of which *n n* and *u*, *'u* are primary, and *i*, *m* are secondary planes.



If bichromate of potash be dissolved in hot dilute nitric acid, a *terchromate* of potash, K.O. . $+3Cr.O_3$, crystallizes when the solution cools.

When bichromate of potash is dissolved in rather more than its own weight of strong muriatic acid, with a very gentle heat, so that no chlorine shall be evolved, and the liquor shall retain its clear orange colour, a salt crystallizes on cooling in fine four-sided prisms, which is very remarkable in constitution, consisting of an equivalent of chloride of potassium united to two of chromic acid, K.Cl. $+2Cr.O_3$.

None other of the chromates of the metals that have been as yet described possess interest.

Vanadium is the basis of several classes of salts, which, however, from the exceeding rarity of the metal, have been but little studied. The salts containing the *vanadic oxide* are generally splendid blue; those containing the *vanadic acid* as basis are red or yellow, while those which contain vanadic acid as acid are colourless, or coloured according to the nature of the base with which it may be combined.

Salts of Tungsten, Molybdenum, Osmium, and Columbium.

Tungsten combines directly with chlorine in two proportions, forming the bichloride and perchloride, according as the metal or the gas is in excess. Both are volatile, and condense in red needles. They are decomposed by water, giving muriatic acid and tungstic oxide, $W.O_2$, or tungstic acid, $W.O_3$. A chlorotungstic acid exists, $W.O_2Cl.$, analogous to the chlorochromic acid.

None of the compounds of tungsten with oxygen act as bases. The nature of the salts of tungstic acid has been sufficiently explained already in p. 374.

Molybdenum takes fire when heated in a stream of chlorine gas, and forms the *terchloride*, $Mo.Cl_3$, which crystallizes in the cold part of the tube in brilliant black scales, like iodine. Its vapour is dark red. Two other chlorides of this metal, Mo. Cl. and $Mo.Cl_2$, are known to exist.

The protoxide of molybdenum forms salts with the oxygen acids, which are purple or black coloured, and are very easily decomposed by heat. Thus the sulphate is resolved into sulphurous acid gas and molybdic oxide. The molybdic oxide also forms a series of salts, generally red coloured, which do not possess any special interest. The molybdic acid forms two series of salts, in one of which it acts as base, and in the other as an acid.

Osmium is the basis of several salts which are as yet very little known. When metallic osmium is heated in a stream of dry chlorine, in a long glass tube, a volatile mixture of protochloride and perchloride of osmium is produced. The former, which is the less volatile, condenses near the heat in long needles of a fine green colour; while the latter, being carried much farther by the current of gas, is deposited as a red powder destitute of any crystalline texture. Both these salts combine with the alkaline chlorides, forming double salts. All three oxides of osmium combine with the oxygen acids to form salts which do not crystallize, and have been very little studied.

Columbium forms a volatile chloride. Its oxide, $Ta.O_2$, does not combine with acids, and the columbic acid forms salts which are not of practical importance.

Salts of Arsenic.

Chloride of Arsenic—$As.Cl_3$; Eq. 2268·0 or 181·74—is formed when the metal burns spontaneously in chlorine; it is a volatile liquid, which forms dense white fumes on exposure to the air. It may be obtained, also, by mixing intimately one part of arsenious acid and three of common salt; putting them into a retort to which a condenser is attached, and adding four parts of oil of vitriol. By a moderate heat the chloride of arsenic distils over as a dense liquid. By much water it is resolved into arsenious and muriatic acids. The sp. gr. of its vapour is 6295.

Iodide of Arsenic, $As.I_3$, is best prepared by digesting one part of arsenic with five of iodine and fifty of water, until the iodine disappears; on cooling, the iodide separates in orange-red crystals. It is decomposed by water into hydriodic and arsenious acids. The bromide of arsenic may be similarly formed.

Arsenic does not form any compound with chlorine, bromine, or iodine analogous to arsenic acid.

Neither compound of arsenic with oxygen is capable of acting as a base, and hence the only classes of salts of arsenious or arsenic acids, are those in which they constitute the electro-negative element.

Arsenious Acid is dissolved in large quantities by the caustic and carbonated alkalies, but the salts thus formed cannot be obtained crystallized, and appear to be very indefinite in constitution. The combinations of arsenious acid with the earths are white powders, of which the only one of interest is *arsenite of Lime*, H.O. . 2Ca.O.+ $As.O_3$, which precipitates when arsenious acid is mixed with lime-water, or arsenite of potash with a salt of lime. It is redissolved by an excess of any acid.

Arsenious acid is decomposed by peroxide of iron, an arseniate of the protoxide being produced; on this is founded the efficacy of the peroxide of iron as an antidote to the poisonous effects of arsenious acid (see p. 384).

The *arsenite of Cobalt* is found native, as a rose-red powder, and the *arsenite of Nickel* exists as a mineral of a pale-green colour; both contain combined water. The arsenites of copper and silver will be described under the heads of these metals, and have been already noticed in p. 381, *et seq*.

The constitution of the salts of arsenic acid has been already mentioned in p. 377. They are all tribasic, and are isomorphous with the corresponding tribasic phosphates. Some of them are of technical and medicinal importance. The neutral arseniate of potash, H.O. . 2K.O.+$As.O_5$, forms a deliquescent saline mass. The *binarseniate of Potash*, 2H.O. . K.O.+$As.O_5$, is formed by adding to the former as much arsenic acid as it already contained, or by igniting in a crucible equal weights of arsenious acid and nitrate of potash; red fumes are given off, and on dissolving the residual mass in boiling water, the salt is obtained in large crystals, which are modifications of the square octohedron.

There are three *arseniates of Soda*, which resemble the three tribasic phosphates of soda. The first, (3Na.O.+$As.O_5$)+24 Aq., is obtained by igniting arsenic acid with an excess of carbonate of soda. When a solution of arsenic acid is neutralized by carbonate of soda, the salt H.O. . 2Na.O.+$As.O_5$ is obtained, which may be had either with 24 Aq. or 14 Aq., according to the temperature at which it crystallizes. The *binarseniate of Soda*, 2H.O. . Na.O.+$As.O_5$, resembles the corresponding salt of phosphoric acid.

The arseniates of the earths are white powders, insoluble in water, but soluble in an excess of any acid.

Arseniates of Iron.—That of the protoxide, H.O. . 2Fe.+$As.O_5$, is a white powder, which, by exposure to the air, gradually becomes green by absorbing oxygen, thereby approaching to the constitution of the native arseniate of iron, in which the iron is in the state of black magnetic oxide. This salt corresponds to the blue phosphate of iron, its formula being (2Fe.O. . H.O.+$As.O_5$)+$2Fe_2O_3$. $As.O_5$+ 12 Aq.

The *perarseniate of Iron* is a white powder, which, when heated, gives off 12 Aq. and becomes red; it has the singular property of dissolving totally in water of ammonia.

Arseniate of Nickel is a pale green powder. *Arseniate of Cobalt* is a rose-red powder, and may be used in place of phosphate of cobalt in preparing Thenard's blue

(p. 417). It is prepared on the large scale by roasting the native arseniuret of cobalt, Co_3As.

The sulphur salts of arsenic are some of the best characterized among that class (p. 379). There are three *sulphoarseniates of Potassium*, having respectively the formulæ ($3K.S.+As.S_5$), ($2K.S.+As.S_5$), and ($K.S.+As.S_5$). They are all deliquescent, and crystallize with water. It would be very interesting to find whether the second and third salts contain basic water, such as would keep up the tribasic character of the first. The *sulphoarseniates of Sodium* resemble those of potassium. The basic salt ($3Na.S.+As.S_5+15$ Aq.) crystallizes in large colourless rhomboidal tables. When orpiment is dissolved in solution of sulphuret of potassium, *sulphoarsenite* of potassium is obtained, $K.S.+As.S_3$, which, when evaporated, is decomposed, and deposites a brown powder, which consists of $K.As.S_3$, and appears to contain a bisulphuret of arsenic, $As.S_2$, combined with K.S., which is decomposed when separated from the state of combination.

Salts of Antimony.

Sesquichloride of Antimony.—$Sb.Cl_3$. Eq. 3383·5 or 271·1. To obtain this salt completely pure, sulphuret of antimony in fine powder is to be mixed with its own weight of corrosive sublimate, and distilled in a hard glass retort. The chloride of antimony distils over with a gentle heat as an oily liquid, which gradually solidifies into a white crystalline mass. It is very deliquescent, and becomes soft on exposure to the air, whence its old name of *Butter of Antimony;* it may be obtained more cheaply for surgical use, but not quite dry, by mixing together two parts of fine common salt and one of crocus of antimony (oxysulphuret, see p. 385), and distilling them in a retort with one part of strong oil of vitriol. Chloride of antimony distils over, and there remains behind sulphate of soda mixed with sulphuret of antimony. In this operation, the crocus antimonii being $2Sb.S_3+Sb.O_3$, the former remains passive; but the latter, acting on $3Na.Cl.$ and $3S.O_3$, produces $Sb.Cl_3$ and $3Na.O..S.O_3$. As there is, however, some water supplied by the oil of vitriol, the product is not solid. It is, however, quite strong enough for its successful application as a caustic.

When chloride of antimony is put in contact with much water, both are decomposed, and a white oxychloride is precipitated, called *Powder of Algarotti*, from the name of its discoverer. If the water be hot, the precipitate is distinctly crystallized. In it one fourth of the metal is combined with chlorine, and three fourths with oxygen; it contains also water, its formula being, according to Berzelius, $Sb.Cl_3+3Sb.O_3+3$ Aq. The formula given by Malaguti and Johnstone is $2Sb.Cl_3+9Sb.O_3$, and it is possible that there are two oxychlorides, which may be produced separately or mixed, according to the circumstances of the precipitation. This oxychloride is employed to furnish oxide of antimony in the preparation of tartar emetic, and of some other salts of antimony.

The terchloride of antimony combines with the chlorides of the alkaline metals, forming double salts, consisting of an equivalent of each constituent.

Perchloride of Antimony, $Sb.Cl_5$, is formed when metallic antimony is burned in chlorine gas. It is a heavy liquid, which fumes in the air, and has a very bad smell; with a small quantity of water it forms crystals (hydrate); with a large quantity of water it gives antimonic and muriatic acids: it is formed, also, by heating sulphuret of antimony in chlorine gas.

The *bromide and iodide of Antimony* are prepared by the direct combination of their elements; the operation does not require external heat; the former is colourless, the latter orange-red. They are both easily fusible, volatile, and decomposed by water.

The sulphurets of antimony act as sulphur acids (p. 387, 388), combining with the sulphurets of the alkaline metals to form double salts, of which several may be crystallized in large rhomboidal tables, perfectly colourless. The basic *hyposulpho-antimonite of Potassium* which remains in solution after the precipitation of Kermes by cooling, crystallizes on evaporation in colourless deliquescent plates.

The sesquioxide of antimony combines with oxygen acids to form salts, which possess but little interest. Metallic antimony decomposes hot oil of vitriol, evolving sulphurous acid gas, and forming the *sulphate of Antimony*, a white salt, which is decomposed by water.

Antimonial Powder. James's Powder.—This preparation, to which, at one time, the highest medicinal virtues were attached, is prepared by mixing together equal parts of sulphuret of antimony and hartshorn shavings, and calcining them together in an iron pot, at a dull red heat, until the mass becomes ash-gray; this is to be then placed in a loosely-covered crucible, and exposed to a white heat for two hours, or until the mass becomes quite white; it is then to be reduced to a fine powder. In this process the sulphur, and the carbon and hydrogen of the hartshorn, are burned away, and the antimony is converted into antimonious acid, of which a small quantity unites with the lime that had been as carbonate in the bone; the rest of the lime remains as phosphate, mixed with the antimonite of lime and the antimonious acid. Its composition varies very much; it seldom contains more than one per cent. of antimonite of lime, which is its only soluble and active principle; and where it has been washed, as is sometimes done, even this is removed. It is also a mere mechanical mixture of its ingredients.

Tartar emetic will be described under the head of tartaric acid and its salts.

Salts of Titanium, Tellurium, and Uranium.

Chloride of Titanium, $Ti.Cl_2$, is best prepared by treating a mixture of titanic acid and lampblack by chlorine, as for the preparation of chloride of silicon. It is a colourless liquid, very volatile, fuming in the air, resembling closely bichloride of tin; it combines with water so violently as to produce explosion, and is decomposed by a large quantity.

There are no oxygen salts of titanium of any interest.

Bichloride of Tellurium, $Te.Cl_2$, is produced by heating tellurium in a current of dry chlorine; a thick liquid is produced, at first dark red, but becoming yellow as it cools, and at last solidifying into a snow-white crystalline mass. This salt is decomposed by water into tellurous and muriatic acids, and combines with the alkaline chlorides to form double salts. The *protochloride* is prepared by melting together equal weights of the bichloride and of tellurium, and distilling; it condenses as a deep yellow liquid, which solidifies, but does not appear crystalline. It forms double salts.

The tellurous acid appears to possess feeble basic properties, as it unites with the strong acids to form compounds which are not important. The relations of tellurous and telluric acids to bases have been already noticed at sufficient length (p. 389).

The *chlorides of Uranium*, $U.Cl.$ and U_2Cl_3, give yellowish green solutions, but do not crystallize. With the alkaline chlorides they unite, forming crystallizable double salts.

Protosulphate of Uranium crystallizes in green prisms.

Sesquisulphate of Uranium, $U_2O_3+3S.O_3$, is not itself crystallizable, but combines with sulphate of potash in several proportions to form double salts of very complex constitution.

The *Sesquinitrate of Uraninm*, $U_2O_3+3N.O_5$, crystallizes in large tabular crystals of a bright yellow colour. This salt is remarkable as the most definite nitrate of a sesquioxide that is known to chemists.

All these salts are prepared by dissolving the oxides of uranium in the dilute acids.

Salts of Copper.

Copper forms two series of salts, one corresponding to the suboxide, and the other to the black oxide. The former are generally white, and the latter blue or green.

Chloride of Copper, Cu.Cl., is produced by dissolving copper in aqua regia, or oxide of copper in muriatic acid. Its solution is green, and it gives, on evaporation, the hydrated salt in long, slender green prisms, Cu.Cl.+2 Aq., which are slightly deliquescent, and are soluble in alcohol. When heated they give off water, and the dry chloride remains as a brown powder, which recombines with water, with the evolution of much heat. Strongly heated, it fuses, gives off half its chlorine, and the *subchloride* remains, melted into a brown resinous-looking mass, whence its name of *resina cupri*. By the action of an alkali on a solution of chloride of copper, an oxychloride may be formed, which precipitates as a fine green powder, having the formula Cu.Cl.+3Cu.O.+Aq., and which is used as a pigment by the name of *Brunswick Green*. There exist two other oxychlorides of copper, which have the formulæ Cu.Cl.+2Cu.O.+3 Aq., and Cu. Cl.+4Cu.O.+6H.O., prepared by the decomposition of the ammoniacal chlorides of copper.

The *Subchloride of Copper*, $Cu_2Cl.$, may be prepared either by heating the chloride as above, or by digesting the clippings of thin copper in a strong solution of chloride of copper, to which some muriatic acid had been added. The liquor gradually acquires an olive colour, and the subchloride is deposited in the form of a white powder. In this case the Cu.Cl. combines with a second equivalent of copper, forming Cu_2Cl. It also precipitates when chloride of copper is acted on by protochloride of tin, 2Cu.Cl. and Sn.Cl. producing $Cu_2Cl.$ and $Sn.Cl_2$. This subchloride is insoluble in water; it dissolves in muriatic acid, which lets it fall by dilution with water. It absorbs oxygen rapidly from the air, and becomes green. It forms with water of ammonia a colourless solution, which rapidly becomes blue on exposure to the air.

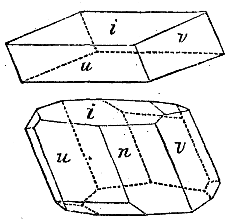
Both chlorides of copper combine with the chlorides of the alkaline metals to form double salts.

The *Bromide* and *Subbromide of Copper*, Cu.Br. and $Cu_2Br.$, resemble in every respect the chlorides just described.

The *Iodide of Copper*, Cu.I., does not appear to exist except in combination. If solutions of iodide of potassium and chloride of copper be mixed, the subiodide is precipitated, while half the iodine is set free, 2Cu.Cl. and 2K.I. producing 2K.Cl. and $Cu_2I.$, with free I. But if an excess of iodide of potassium be added, these elements recombine, and a double salt, Cu.I.+K.I., may be obtained. The preparation of the subiodide of copper just given involves the loss of an atom of iodine, which is avoided by previously mixing the liquor with an excess of solution of protosulphate of iron, by which the copper salt is reduced to the state of suboxide, and all the iodine then precipitated as subiodide. Thus made, it is a pale yellow powder, unaltered by the air.

Sulphate of Copper.—Cu.O. . $S.O_3$. H.O.+4 Aq. Eq. 996·9+562·5 or 79·9+45. For the purposes of the arts, in which this salt is extensively employed, it is prepared by treating the native sulphuret of copper in the manner described under the head of the sulphates of iron and zinc. It may also be obtained by boiling oil of vitriol on metallic copper, when sulphurous acid gas is given off, or by acting on the metal with dilute sulphuric acid, to which some nitric

acid had been added. It crystallizes in large doubly-oblique rhombs, of a fine blue colour, whence its name, *Blue Vitriol.* In the



figure, the primary rhomb and the most usual secondary form are given, *i*, *u*, *v* marking the primary planes in each. These crystals dissolve in four parts of cold and two of boiling water. Of the five atoms of water which it contains, one is constitutional, and may be replaced by the alkaline sulphates, to form a class of double salts of great beauty. By the action of a small quantity of ammonia, a *basic sulphate* is obtained, of which the formula is $Cu.O..S.O_3+3Cu.O.+4\ Aq.$; and another, containing $Cu.O..S.O_3+7Cu.O.+12\ Aq.$, is occasionally observed to form.

Nitrate of Copper.—$Cu.O..N.O_5+3\ Aq.$ This salt is obtained when copper is dissolved in dilute nitric acid; it crystallizes in oblique rhombs of a rich blue colour, and sometimes in paler rhomboidal plates, which contain 6 Aq. This salt deflagrates violently when thrown on burning coals, or when struck on an anvil with a little phosphorus. If some of it be wrapped up tight in tin foil, it becomes very hot, swells up, fumes, and oxidizes the tin so rapidly, that in some points brilliant sparks are thrown out. When heated above 200°, it loses acid, and a basic nitrate remains, which may also be formed by adding a small quantity of ammonia to a solution of the neutral salt. The formula of the basic salt is $H.O..N.O_5+3Cu.O.$

Phosphate of Copper, $H.O..2Cu.O.+P.O_5$, and the *arseniate of Copper*, $H.O..2Cu.O.+As.O_5$, are pale green powders, obtained by double decomposition.

Arsenite of Copper, $H.O..2Cu.O+As.O_3$, is obtained by the decomposition of arsenite of potash and sulphate of copper: it is a fine apple-green powder, the importance of which, as a test for arsenic, has been already discussed (p. 381). It is employed in the arts, under the name of *Scheele's Green*, as a pigment, and is prepared on the large scale by dissolving two pounds of pure sulphate of copper in twelve quarts of water, previously heated in a copper pan. In another pan two pounds of pure calcined pearlash are dissolved, with eleven ounces of arsenious acid, in four quarts of pure water. Both liquors are strained through linen, and then the arsenical solution is gradually added to the solution of copper. The precipitate is collected on a cloth and carefully dried. The produce should be 1 lb. 6½ oz. A still more beautiful pigment, which may be best described here, is prepared under the name of *Schweinfurt Green*, or *Emerald Green;* it is a compound of acetate of copper and arsenite of copper, $Cu.O..\overline{A}+3(H.O..2Cu.O.+As.O_3)$. It is prepared by mixing up ten parts of pure verdigris with as much hot water as will make it into a thin pulp, and straining it through a sieve to separate the impurities: nine or ten parts of arsenious acid are to be then dissolved in 100 parts of boiling water, and while boiling, the verdigris pulp is to be gradually added thereto, continually stirring. At first a mere arsenite of copper falls, and all the acetic acid remains in the liquor; it being only after much agi-

tation that the double salt is produced, which is known by the light flocculent precipitate changing into a heavy granular powder of a brilliant green colour.

The salts of the suboxide of copper with the oxygen acids possess no practical interest.

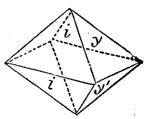
Salts of Lead.

Chloride of Lead, Pb.Cl., may be produced by boiling lead in strong muriatic acid, or by acting on oxide of lead with the same acid; but more simply by adding to any soluble salt of lead a solution of chloride of sodium. A curdy white precipitate falls, which dissolves in boiling water, and, on cooling, crystallizes in opaque plates of a pearly lustre, which do not contain water. This salt requires 135 parts of cold water to dissolve it, but is much more soluble in boiling water. It is easily fused, and, on cooling, forms a semi-transparent mass like horn, whence the old name, *plumbum corneum*. By the action of ammonia on chloride of lead, several *oxychlorides* may be formed, of which none are now of interest.

Bromide of Lead resembles perfectly the chloride.

Iodide of Lead, Pb.I., is formed by adding iodide of potassium to a solution of nitrate of lead; a bright lemon-yellow precipitate falls, which requires 1235 parts of cold, and but 194 of boiling water to dissolve it. The solution is colourless, and, on cooling, deposites the iodide of lead in splendid gold-coloured six-sided plates, which maintain their metallic lustre perfectly in drying. The iodide of lead forms double salts with the alkaline iodides, and gives, with ammonia, oxyiodides when the alkali is not in excess.

Sulphate of Lead.—Pb.O..S.O_3. This salt is found in the mineral kingdom in large transparent rhombs, isomorphous with sulphate of barytes, and of which the octohedron *i*, *y*, in the figure, is the primary form. It may be also formed by adding to any solution containing lead sulphuric acid or a sulphate. It falls down as a white powder, which, from its insolubility, furnishes a good test for lead. When strongly ignited, it melts without decomposition, but with charcoal it is reduced to sulphuret of lead. The sulphate of lead is soluble in strong acids; and hence the oil of vitriol, manufactured in leaden chambers, generally contains a small quantity of it dissolved, which is precipitated on the addition of water.



Nitrate of Lead, Pb.O..N.O_5, is obtained by dissolving lead in dilute nitric acid, and evaporating. It crystallizes in regular octohedrons, often modified, which are generally opaque; it is soluble in seven and a half parts of cold, and much less of boiling water. It is not soluble in nitric acid. When heated, it gives out a mixture of oxygen and nitrous acid gases (p. 276), and leaves melted protoxide of lead. By the action of ammonia, a series of basic salts are obtained, which contain two, three, and six atoms of oxide of lead united to one of nitric acid.

When a solution of nitrate of lead is boiled on finely-divided metallic lead, this dissolves, and on cooling, brilliant yellow plates are deposited, which are *basic nitrite of Lead*, 2Pb.O.+N.O_4. By adding sulphuric acid to a solution of this salt, a neutral nitrite is

obtained, $Pb.O..N.O_4+H.O.$, which crystallizes in yellow octohedrons. If an excess of lead be used in the preparation of the nitrite, the acid is still farther deoxidized, and a *hyponitrite of Lead*, $3Pb.O.+N.O_3+3$ Aq., is produced, which crystallizes in rose-red scales. These salts are of interest, as it was doubted whether the nitrous acid ($N.O_4$) could combine with bases, and it is only in these cases that we have obtained positive evidence of its doing so, which we owe to Peligot.

Phosphate of Lead, $H.O..2Pb.O.+P.O$, is formed by the action of common tribasic phosphate of soda on a solution of nitrate of lead; it is a white powder, which is changed by ammonia into $3Pb.O.+P.O_5$.

Silicate of Lead has been noticed in relation to crystal and to flint glass.

Chromate of Lead—$Pb.O..Cr.O_3$.—*Chrome Yellow* is formed by mixing together solutions of nitrate of lead and bichromate of potash. It precipitates as a fine lemon-yellow powder, insoluble in water. It occurs native in ruby-red crystals, constituting the *red lead ore*. This salt is manufactured largely for a pigment, which is found of various shades of yellow and orange in the market, being mixtures of the true neutral chromate, prepared as above, with the *basic chromate of Lead*, $2Pb.O.+Cr.O_3$, which is of a bright vermilion colour, and is termed *Chrome Red*. This may be prepared by adding potash to a solution of chromate of potash until this reacts strongly alkaline, and then mixing it with nitrate of lead, or by digesting the neutral chromate of lead in a warm solution of potash, which removes half the acid. These give products, however, inferior in brilliancy of tint to the following. Saltpetre is to be melted in a crucible at a dull red heat, and chrome yellow gradually added thereto, as long as effervescence, with escape of red fumes, occurs. The potash abandons the nitric acid and takes half the chromic acid, and basic chromate of lead is formed. The mass becomes black, and is then to be allowed to settle, and the melted salt poured off from the heavy powder at the bottom; this, when cold, becomes of a splendid vermilion red, and is to be taken out and washed with the smallest possible quantity of water.

Salts of Bismuth.

Chloride of Bismuth, Bi_2Cl_3, is formed by dissolving bismuth in hot strong muriatic acid; by evaporation it forms a crystalline mass which is very deliquescent, volatile, and fusible. By water it is decomposed, giving the oxychloride of bismuth, a white powder, having the composition $Bi_2Cl_3+2Bi_2O_3+3H.O.$ In the arts this powder is sometimes employed under the name of *Spanish White* or *Pearl White*.

The chloride of bismuth combines with the chlorides of the alkaline metals, forming double salts, in which the chlorine combined with the bismuth is to that combined with the other metal as three to two. In the double salts formed by protochlorides, this relation is never observed, and hence it furnishes additional proof that the chloride of bismuth is a sesquichloride, on which idea the formulæ become $2K.Cl.+Bi_2Cl_3+2$ Aq. and $2Na.Cl.+Bi_2Cl_3+3$ Aq.

Sulphate of Bismuth, $Bi_2O_3+3S.O_3$, is formed by dissolving bismuth in hot sulphuric acid. It forms a deliquescent mass of acicular crystals, which are decomposed by water, giving a white powder, the *basic sulphate of Bismuth*, $Bi_2O_3+S.O_3$.

The *Nitrate of Bismuth*, $Bi_2O_3+3N.O_5+9$ Aq., is formed by dissolving the metal in dilute nitric acid; by evaporation and cooling rhomboidal crystals are obtained, which easily deliquesce; when heated, they lose water and nitric acid, and form a basic salt, and finally oxide of bismuth remains behind. Like the other salts of bismuth, this is decomposed by water, and may produce one or other of two basic salts, according to circumstances. When the crystals, without any excess of acid, are decomposed by water, the precipitate has the composition $4Bi_2O_3+3N.O_5+9H.O.$; while, if an acid liquor be decomposed by water, the precipitate has the formula $Bi.O_3+N.O_5$. Both of these salts yield very nearly the same quantity of oxide of bismuth on analysis, and were hence long confounded together. Many reasons for considering the oxide of bismuth to be a sesquioxide have been given (p. 398). These subnitrates of bismuth are used indiscriminately in medicine, but the latter form is more generally found in the shops. The names *Pearl White*, &c., are also applied to these bodies.

Salts of Silver.

Chloride of Silver—Ag.Cl.; Eq. 1794·3 or 143·8—exists native as an ore of silver, *horn silver*, and may be formed by mixing a solution of common salt with a soluble salt of silver. It forms a curdy white precipitate, perfectly insoluble in water and in acids, but easily soluble in water of ammonia. When heated, it fuses below redness, and on cooling, congeals into a semitransparent mass of a horny aspect, whence its old name. When freshly precipitated, it is exceedingly sensible to the action of light, becoming pink, violet, and ultimately black by exposure to the sun's rays; but for this reaction, it is necessary that organic matter or water should be present, with the hydrogen of which the chlorine may combine, and that thus a thin layer of subchloride or of metal may be produced. The relations of chloride of silver to light are of the highest importance in photography, and in examining the structure of the solar rays, as noticed in p. 173, *et seq.* The processes for the reduction of chloride of silver to the metallic state have been described in p. 399, 400.

Iodide of Silver, Ag.I., is obtained by decomposing a soluble salt of silver by iodide of potassium; a primrose-yellow precipitate falls, which is insoluble in water and in ammonia; at least it requires 2500 parts of strong water of ammonia to dissolve one of iodide of silver. It is easily fusible, and becomes opaque on cooling. In certain forms it is still more sensible to light than the chloride, and is hence the basis of the impression in the photographic process of Daguerre (see p. 175). It is reduced to the metallic state by the same means as the chloride.

Bromide of Silver, Ag Br., resembles the chloride in every particular respect.

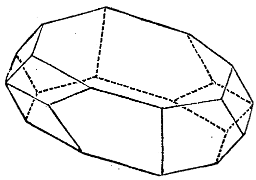
Sulphate of Silver, Ag.O. . $S.O_3$, is formed by boiling metallic sil

ver in oil of vitriol; sulphurous gas is given off, and a white saline mass formed, which, when more strongly heated, is totally decomposed, leaving metallic silver. This salt dissolves in eighty-eight parts of boiling water, and crystallizes, on cooling, in small needles.

Hyposulphite of Silver.—$2Ag.O.+S_2O_2$. The relations of hyposulphurous acid to oxide of silver are very curious. On adding a neutral solution of nitrate of silver to a solution of hyposulphite of soda, a white precipitate appears, which at first redissolves, but subsequently becomes permanent. It soon loses its pure colour, especially if heated, and at last becomes black from sulphuret of silver, while the liquor contains sulphate of silver; thus $2Ag.O.+S_2O_2$ produce $Ag.S.$ and $Ag.O..S.O_3$. The solution of this salt is extremely sweet. So great is the affinity of hyposulphurous acid to oxide of silver, that a solution of it dissolves chloride of silver, forming an intensely sweet liquor; and the solutions of the alkaline and earthy hyposulphites dissolve all the salts of silver insoluble in water, except the arseniate and the iodide, and form double salts of exceedingly sweet taste. The double hyposulphites contain generally one equivalent of hyposulphite of silver to two of the other salt, but our knowledge of these salts is not, as yet, by any means complete.

Nitrate of Silver.—$Ag.O..N.O_5$. Eq. 2128·5 or 170·57. This is the most important salt of silver; it is manufactured on a very large scale in the Apothecaries' Hall of Ireland for medicinal use.

It is prepared by dissolving granulated silver in dilute nitric acid, which at first occurs without the disengagement of any gas, as the nitric acid dissolves the nitric oxide formed, but towards the end copious red fumes are evolved. By evaporation and cooling, the salt is obtained in colourless rhomboidal plates, as in the figure,



often four inches across, which are anhydrous. It is soluble in its own weight of cold water. When heated to about 430°, it melts into a colourless liquid, which is poured into cylindrical silver moulds, and congealing, forms the sticks of *lunar caustic* used in surgery. This fused salt should be snow-white; it is not affected by light unless organic matter be present, as has been fully shown by Scanlan; but with organic matter it soon becomes quite black, silver being reduced. It is hence used as marking ink, and for staining hair black. When strongly heated, nitrate of silver is totally decomposed. It yields its oxygen readily to combustible bodies; thus, if a few grains of it be laid on an anvil with a little bit of phosphorus, and struck with a hammer, it explodes violently. Its solution is reduced to the metallic state by all deoxidating agents.

Hyponitrite of Silver, $Ag.O..N.O_3$, is obtained in granular crystals by adding the soda salt prepared by melting nitrate of soda (p. 428) to a boiling solution of nitrate of silver, and filtering while very hot.

Tribasic Phosphate of Silver, $3Ag.O.+P.O_5$, is the canary-yellow precipitate, produced by adding a tribasic phosphate of soda to a solution of nitrate of silver. Its relations to the other phosphates

of silver, and to the silver test for arsenic, have been noticed in p. 298 and 381.

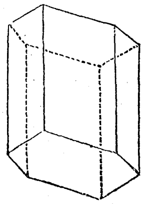
Arseniate of Silver, $3Ag.O.+As.O_5$, is precipitated as a reddish-brown powder on adding any solution of an arseniate to a solution of nitrate of silver. Its formation is one of the most characteristic properties of arsenic acid.

Arsenite of Silver, $H.O. . 2Ag.O. +As.O_3$, is produced, as has been noted in p. 401, by adding a solution of arsenious acid to the ammoniacal nitrate of silver, or of arsenite of potash to nitrate of silver. It is a canary-yellow powder, soluble in ammonia and in nitric acid. When heated, it first yields water and becomes brown; then it gives oxygen, arsenious acid, and leaves metallic silver.

Salts of Mercury.

Chloride of Mercury. Corrosive Sublimate—$Hg.Cl.$; Eq. 1708·5 or 136·9—may be prepared by dissolving red oxide of mercury in muriatic acid, and evaporating. It crystallizes in long right-rhombic prisms, generally opaque. It may also be very economically prepared by dissolving the basic sulphate (turpeth mineral) in strong muriatic acid, and crystallizing; the sulphate of mercury remains in the mother liquor, and may be again converted into basic sulphate by the action of water. The corrosive sublimate is, however, generally prepared, for pharmaceutic purposes, by the dry way, as follows: sulphate of mercury, $Hg.O. . S.O_3$, is to be well mixed with its own weight of common salt, $Na.Cl.$, and the mixture introduced into a wide-necked glass retort, or, on the large scale, into a stoneware pot, to which a globular glass head is attached. The retort or pot, being bedded in sand, is gradually heated to redness; decomposition occurs, the chlorine of the common salt combining with the mercury, while the sodium takes the oxygen and acid; we have therefore formed $Hg.Cl.$, which sublimes into the head, forming a mass of prismatic crystals, which, being partly fused by the heat, cohere strongly together, and sulphate of soda, which remains behind; $Hg.O. . S.O_3$ and $Na.Cl.$ giving $Hg.Cl.$ and $Na.O. . S.O_3$.

The sublimed chloride of mercury crystallizes in a right-rhombic prism, as represented in the figure. Its specific gravity is 5·4; it melts at 509°, and boils at 563°. The specific gravity of its vapour is 9420. It dissolves in two parts of boiling and in twenty of cold water; the hot solution crystallizes, on cooling, in prisms of a different form from that of the sublimed salt; it is therefore dimorphous; it is soluble in $2\frac{1}{3}$ parts of cold alcohol, and in three parts of cold ether; it dissolves much more readily in muriatic acid and in solutions of the alkaline chlorides than in pure water, as it forms with these bodies double salts, which are very soluble; of these, the double chloride of mercury and ammonium, *sal alembroth*, is employed in pharmacy. It will be specially described hereafter. A solution of corrosive sublimate yields all the reactions of a salt of the red oxide of mercury, described in p. 403. When a small quantity of potash is added to a solution of sublimate, a brown precipitate falls, which by boiling becomes black and crystalline; the same substance may be

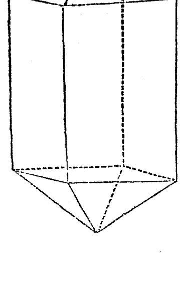


formed by boiling red oxide of mercury in a solution of sublimate; it is an *oxychloride of mercury*, whose formula is Hg.Cl.+3Hg.O.

If a solution of sublimate be treated by a small quantity of sulphuret of hydrogen, a precipitate forms, at first brownish, but which ultimately becomes quite white, provided there be sublimate in excess; it is a *chlorosulphuret*, of which the formula is Hg.Cl.+2Hg.S.

Subchloride of Mercury. Calomel.—Hg_2Cl. Eq. 2974·3 or 238·3 This important medicinal agent may be prepared either by precipitation or by sublimation. For the former object, nine parts of mercury are to be digested in eight parts of nitric acid, sp. gr. 1·25, without heat, until no more mercury appears to dissolve, and the liquor begins to assume a yellow colour; eight parts of common salt are next to be dissolved in 250 parts of boiling water, to which a little muriatic acid may be added: these solutions being mixed, the calomel immediately precipitates, and thus prepared, it is absolutely pure. The mercury dissolving in the nitric acid, forms nitrate of the suboxide, and by the chloride of sodium, nitrate of soda and subchloride of mercury are formed; Hg_2O. . $N.O_5$ and Na.Cl. giving Hg_2Cl. and Na.O. . $N.O_5$.

To obtain calomel by sublimation, four parts of corrosive sublimate may be rubbed up with three parts of mercury, so intimately that no trace of metal shall be visible; and the mixture being introduced into an earthen pot to which a glass head is fitted, heat is to be gradually applied until the materials have all sublimed. In this operation, Hg.Cl. combining directly with Hg., gives Hg_2Cl. The union is never perfected by the first sublimation, and the product is to be again powdered, well mixed, and again sublimed. The process followed by the British pharmacopœias is different, and is best carried on in the following proportions: Thirty-one parts of dry sulphate of the red oxide of mercury (persulphate) are to be intimately mixed with twenty and one third parts of metallic mercury and twenty parts of fused common salt, and the whole rubbed together until the mercurial globules totally disappear. This method is the same as the former in principle, except that the corrosive sublimate is generated only when required to combine with the additional quantity of mercury to form calomel. The sublimation is carried on as described above. The sublimed mass is always contaminated with some undecomposed sublimate. Hence it must be carefully levigated, and washed with boiling water as long as the washings give any milkiness on the addition of a few drops of water of ammonia.



The precipitated calomel is a pure white powder. When sublimed, it forms a crystalline mass, whose primitive form, as in the figure, is a square prism. It is insoluble in water; and the minute division of the sublimed calomel may be elegantly secured by conducting its vapour into a vessel containing boiling water, by the vapour of which it is suddenly condensed, and falls as an excessively fine powder. Its specific gravity is 6·5. The presence of sublimate in the calomel of the shops is detected by boiling for a few minutes in alcohol, and adding to the alcoholic li-

quor some water of ammonia, which gives a white precipitate if corrosive sublimate be present. By boiling with muriatic acid, or with solution of common salt or sal ammoniac, calomel is gradually decomposed into sublimate, which dissolves, and metallic mercury, which remains behind.

The Bromide and Subbromide of Mercury, Hg.Br. and $Hg_2Br.$, may be prepared, the first by acting directly on mercury with bromine, when a colourless solution is obtained, which gives prismatic crystals by evaporation; the second, by decomposing nitrate of the suboxide by bromide of potassium. These bodies resemble completely sublimate and calomel in their properties.

Iodide of Mercury. Red Iodide—Hg.I.; Eq. 2845·0 or 228·0—may be formed by the direct combination of its elements, even without heat, by trituration together with a few drops of alcohol. It is then dark red, but may be obtained of a brilliant red colour by precipitating a solution of corrosive sublimate with an equivalent of iodide of potassium. An excess of the latter redissolves the precipitate, as it forms a double salt (K.I.+Hg.I.), soluble in water, and crystal lizable in octohedrons. The iodide of mercury is insoluble in water; when heated, it fuses and sublimes, condensing in a crystalline mass, formed of rhomboidal plates, which, when broken or scratched, gradually become red, breaking up into a number of minute crystals of a different form. It is somewhat soluble in alcohol, and abundantly in aqueous hydriodic acid. A hot solution of iodide of potassium dissolves much more than the atomic proportion of it; the excess crystallizes in long, red, square prisms, according as the solution cools. It dissolves also in a strong solution of corrosive sublimate, with which it combines in two proportions. It forms a class of double salts, equally extensive with that produced by corrosive sublimate.

Subiodide of Mercury, $Hg_2I.$, may be formed by triturating iodine with mercury, or by precipitating a solution of iodide of potassium by a slight excess of nitrate of the suboxide of mercury. It is an olive-green powder, which is resolved by heat into metallic mercury and iodide, and is similarly decomposed by a solution of iodide of potassium, with which the iodide of mercury formed combines.

Sesquiodide of Mercury, or *Yellow Iodide.*—Hg_4I_3 or $2Hg.I. + Hg_2I.$ To obtain this substance, a solution of iodide of potassium, to which half as much iodine as it already contained has been added, is to be decomposed by a slight excess of a solution of the subnitrate of mercury. The bright yellow powder which precipitates must be dried cautiously with little exposure to light. By means of a solution of iodide of potassium, it is resolved into red iodide and metallic mercury. The reaction by which it is formed is that, of the subiodide first produced, by the K.I. and $Hg_2O.\ .\ N.O_5$, one half is converted into red iodide by the additional atom of iodine which is supplied; $2(K.I.)+I.$ and $2(Hg_2O.\ .\ N.O_5)$ giving $2(K.O.\ .\ N\ O_5)$ and $Hg_2I. + 2Hg.I.$ This preparation is employed in pharmacy.

A preparation which has been proposed by Donovan, under the name of *Iodo-hydrargyrate of Arsenic*, is prepared by rubbing together 6·08 grs. arsenic, 15·38 grs. of mercury, and 50 grs. iodine, with a few drops of alcohol, until they combine, and then adding eight ounces of water with a few drops of hydriodic acid; a solution is obtained, at first colourless, but soon becoming yellowish-brown by

light, from iodine being set free. This preparation is not a cnem ical compound; but the iodide of arsenic being decomposed by the water, the iodide of mercury is dissolved by the hydriodic acid formed, while arsenious acid exists free in the solution.

Sulphate of Mercury—$Hg.O..S.O_3$; Eq. 1867 or 149·6—is produced by boiling oil of vitriol on mercury, until it is converted into a white saline mass, which requires to be finally heated nearly to redness to expel the excess of acid. Sulphurous acid is evolved, Hg. and $2S.O_3$ giving $Hg.O..S.O_3$ and $S.O_2$; but this may be avoided by adding from time to time a small quantity of nitric acid, by which oxygen will be supplied. This salt forms a white powder, not crystalline; at a full red heat it is resolved into mercury, sulphurous acid, and oxygen. Its use is extensive in preparing calomel and sublimate. By a large quantity of water it is decomposed into free acid and *basic sulphate, turpeth mineral*, $3Hg.O.+S.O_3$, which is a bright yellow powder, which, when heated with muriatic acid, gives neutral sulphate and corrosive sublimate, $2H.Cl.$ and $(3Hg.O.+S.O_3)$ producing $2Hg.Cl.$ and $Hg.O..S.O_3$, water being formed (see p. 461).

Subsulphate of Mercury—$Hg_2O..S.O_3$—*Sulphate of the Black Oxide* may be formed by heating metallic mercury with oil of vitriol, provided the heat do not pass beyond 212°; or by mixing strong solutions of nitrate of the black oxide and of sulphate of soda. It is a white powder, very sparingly soluble in water, by which it is not decomposed, and is thereby distinguished from the preceding salt.

Nitrate of Mercury. Nitrate of the Red Oxide.—$2Hg.O..N.O_5+2\ Aq.$ This salt is formed when mercury is dissolved in an excess of nitric acid with heat. It crystallizes in rhomboidal plates, which are deliquescent, and soluble in a small quantity of water. Its solution is decomposed when diluted, a *basic nitrate of the Red Oxide* being precipitated of a bright canary colour, and having the formula $H.O..N.O_5+3Hg.O.$ If this powder be boiled with much water, a still more basic salt is formed, which has the formula $N.O_5+6Hg.O.$ Both this salt and the sulphate, when heated by sulphuretted hydrogen not in excess, give white basic compounds, like the chlorosulphuret (p. 464), having the formulæ $Hg.O..N.O_5+2Hg.S.$ and $Hg.O..S.O_3+2Hg.S.$

Subnitrate of Mercury. Nitrate of the Black Oxide.—When mercury is dissolved in dilute nitric acid, without any heat, or with only as much as sustains a very moderate action, the black oxide forms, and may unite with the nitric acid in various proportions. 1st. If there be nitric acid in excess, the solution gives by cautious evaporation clear transparent rhombs of *neutral subnitrate*, having the formula $Hg_2O..N.O_5+2H.O.$ 2d. If there be an excess of mercury, large opaque white rhombic prisms sometimes form, which have the composition $(3Hg_2O.+2N.O_5+3H.O.)$. 3d. By letting this solution stand, these crystals gradually disappear, and very small canary-yellow crystals, nearly spherical, with numerous brilliant facets, are produced: this is a basic salt, the formula being $H.O..N.O_5+2Hg.O.$ This salt may also be formed by the action of water on either the first or second; both being decomposed into free acid, and the

basic salt, which is not farther altered even by boiling water. The second salt may be looked upon as a compound of the first and third, since $(3Hg_2O.+2N.O_5+3H.O.)=(Hg_2O..N.O_5+2H.O.)+(H.O..N.O_5+2Hg_2O.)$.

Subchromate of Mercury, $Hg_2O.+Cr.O_3$, produced by mixing solutions of chromate of potash and subnitrate of mercury, is a bright orange powder, insoluble in water; when heated to redness, it gives off mercury and oxygen, and chromic oxide of a fine green colour remains (p. 372).

Red nitrate of mercury combines with iodide of mercury to form a double salt, which is formed by half precipitating a solution of the mercuric salt by iodide of potassium, and boiling until the precipitate redissolves; on cooling, the new salt is deposited in brilliant red crystalline scales, which are decomposed by much water.

Salts of Gold.

Perchloride of Gold.—$Au.Cl_3$. When gold is dissolved in nitromuriatic acid, and the solution evaporated very cautiously to dryness, this salt remains as a ruby-red crystalline mass, which dissolves with a yellowish-red colour in water. Its solution is acid, and is decomposed by the light, and by all deoxidizing agents. It combines with muriatic acid, and forms a deep yellow liquor, from which the *acid chloride of Gold* crystallizes in long yellow needles. It is soluble in alcohol and in ether, from which last solution it is deposited in the metallic state on evaporation, the chlorine combining with the ether. In this way some forms of gilding are effected, as on steel. The chloride of gold combines with many other chlorides, forming double salts. The chloride of gold and potassium, $Au.Cl_3+K.Cl.+5$ Aq., crystallizes in orange-red striated rectangular prisms. It effloresces in the air, and may be obtained anhydrous; it is then ruby-red. Chloride of gold and sodium ($Na.Cl.+Au.Cl_3+4$ Aq.) forms crystals of the same form and colour, but which do not effloresce: when heated, they fuse in their water of crystallization.

Subchloride of Gold, $Au.Cl.$, is produced by heating the chloride to about 450° in a porcelain dish, stirring it very carefully until no more chlorine is given off. It is a yellowish-white mass, insoluble in water, by which it is gradually decomposed into chloride and metallic gold. It is in this way only that a solution of chloride of gold perfectly free from an excess of acid can be obtained.

Iodides of Gold.—When solutions of chloride of gold and iodide of potassium are mixed, a greenish precipitate occurs of *subiodide of Gold*, $Au.I.$, while two thirds of the iodine become free. If the iodide of potassium be in great excess, however, the iodine and subiodide are both redissolved, and a double salt obtained, which crystallizes, and which contains *iodide of Gold;* its formula is $K.I.+Au.I_3$; by the cautious addition of chloride of gold to a solution of this salt, a greenish precipitate may be obtained without any liberation of iodine, and which hence must be the iodide.

The oxides of gold do not act as bases, and the general nature of the salts which they form, as acids, has been noticed in p. 406.

Salts of Palladium.

Chloride of Palladium, $Pd.Cl.$, is formed by dissolving palladium in nitromuriatic acid. Its solution is deep brown, and it forms, by evaporation, a crystalline mass; by the action of a small quantity of caustic alkali, a basic salt, or *oxychloride of Palladium*, $Pd.Cl.+3Pd.O.+4$ Aq., is produced; it is a brown powder, insoluble in water. The chloride of palladium combines with other chlorides to form double salts: when heated to about 600°, it abandons half its chlorine, and *subchloride of Palladium* remains, an olive-brown powder insoluble in water. By a strong red heat this is totally decomposed.

Deutochloride of Palladium, $Pd.Cl_2$, is formed when the chloride of palladium is gently heated with aqua regia; it forms a dark brown liquor, which gives, with a

solution of chloride of potassium, a sparingly soluble double salt, $K.Cl.+Pd.Cl_2$. This deutochloride cannot be obtained solid, its solution giving off chlorine, and chloride remaining.

Iodide of Palladium, Pd.I., is a black powder, obtained by double decomposition. It forms double salts with other iodides. By heat it is decomposed, without forming any subiodide.

Sulphate of Palladium, $Pd.O..S.O_3$, is produced by dissolving the metal in a mixture of nitric and sulphuric acids. By evaporation, a saline mass is obtained, which is decomposed by water.

Nitrate of Palladium, $Pd.O..N.O_5$, is obtained by acting on the metal with nitric acid. At first it dissolves without any evolution of gas, forming a deep olive liquor; but when heated, it gives off $N.O_2$, and becomes brown. The nitrate of palladium is decomposed by water, giving basic salts.

Salts of Platinum.

Protochloride of Platinum, Pt.Cl., is formed by exposing the bichloride, in fine powder, to a temperature of about 500° in a porcelain dish, and frequently stirring; one half of the chlorine being evolved, a greenish olive powder is produced, which is the protochloride. It is insoluble in water; by a red heat it is resolved into chlorine and metallic platinum. If the bichloride be exposed only to a temperature of about 400°, water dissolves from out of the resulting mass, a substance which colours it intensely brown, and which is, probably, a sesquichloride, Pt_2Cl_3.

Bichloride of Platinum.—$Pt.Cl_2$. This salt is produced by dissolving platinum in nitromuriatic acid. The solution, when free from excess of acid, is intensely yellow; on evaporation, it gives a crystalline deliquescent mass. This salt is very soluble in alcohol, and is so used for the detection of potash (p. 339). It combines with other chlorides, forming double salts, of which some possess considerable interest. Those with chloride of potassium, $K.Cl.+Pt.Cl_2$, and with sal ammoniac, $N.H_4Cl.+Pt.Cl_2$, are precipitated as yellow powders from strong solutions, or as minute octohedral orange-red crystals from dilute solutions of those alkalies, and are hence used for their detection. These salts are insoluble in alcohol. The sodium double salt ($Na.Cl.+Pt.Cl_2$) is, on the contrary, easily soluble both in alcohol and water.

The *Iodides of Platinum* are black powders, insoluble in water, formed by the double decomposition of iodide of potassium with the respective chlorides. The biniodide combines with iodide of potassium to form a double salt $K.I.+Pt.I_2$, which dissolves in water, giving a solution so deeply claret-coloured that it may serve to detect a very minute trace of platinum in solution.

Although many oxygen salts of platinum are described in the systematic books (sulphate, nitrate, &c.), I consider that we possess no accurate knowledge whatever of that class of combinations.

Salts of Iridium and Rhodium.

There are four chlorides of iridium. The *protochloride*, Ir.Cl., is prepared by heating metallic iridium to redness in chlorine; it is an olive-green body, which is insoluble in water, but combines with other chlorides to form double salts. The *sesquichloride*, Ir_2Cl_3, is formed by dissolving the sesquioxide in muriatic acid. It is a brown crystalline substance, volatile, and forming double salts. The *bichloride*, $Ir.Cl_2$, is produced when a concentrated solution of the former is treated with aqua regia. It forms a dark brown solution, giving, when dried, a black mass. It gives with chloride of potassium a sparingly soluble double salt in black octohedral crystals. The *perchloride*, $I.Cl_3$, is not known except in the state of a double salt, $K.Cl.+I.Cl_3$, which is produced by processes, for which I refer to the larger systematic works.

The protoxide, sesquioxide, and deutoxide of iridium form salts with the oxygen

acids; the solutions of the first class being green or purple, those of the second class blood-red, and those of the third orange, produce the variety of tints which gives the name *Iridium* to the metal; they are not otherwise important.

Sesquichloride of Rhodium, R_2Cl_3, is prepared by decomposing the double chloride of rhodium and potassium by hydrofluosilicic acid. The filtered liquor gives, when evaporated, a brown-red mass, destitute of crystalline structure; by heat it is completely decomposed. It combines with other chlorides to form well-defined double salts, such as that $2K.Cl.+R_2Cl_3+2$ Aq. formed by acting on metallic rhodium and chloride of potassium by aqua regia. When metallic rhodium alone is treated by chlorine, a rose-red powder is obtained, insoluble in water and acids, which is a similar compound of protochloride and sesquichloride of rhodium, $R_4Cl_5=2R.Cl.+R_2Cl_3$.

By igniting metallic rhodium with bisulphate of potash, a double salt is obtained, which does not crystallize. The nitrate of rhodium is a dark red deliquescent salt, which gives with nitrate of soda a double salt in dark red crystals.

CHAPTER XVI.

ON THE GENERAL PRINCIPLES OF THE CONSTITUTION OF ORGANIC BODIES.

Organic bodies are distinguished generally by a much greater complexity of composition than occurs in substances of mineral origin. Except in the case of carbonic oxide, there is no example of an atom of an organic compound containing but two simple atoms; and carbonic acid and cyanogen are the only examples of an organic atom being formed by three elementary atoms. On the contrary, the number of simple atoms entering into the composition of an organic body is sometimes very great: thus an equivalent of oleic acid contains 270 simple atoms; an atom of albumen is formed of 883 simple atoms; an atom of spermaceti includes 468 simple atoms; numbers to which we find no form of combination approaching in inorganic compounds.

Besides this greater complexity of constitution, organic bodies are distinguished by the nature of their elements. I have had occasion already to describe as inorganic fifty-four undecompounded bodies, which, by their reunion in various proportions, generate the compound substances which constitute the mineral crust of the globe; but among organic bodies we meet with few of these. Although equalling in number and surpassing in variety of properties the mineral species, the products of the animal and vegetable kingdom may be looked upon as consisting almost exclusively of six elements, of which two, sulphur and phosphorus, are met with but seldom; nitrogen is much more extensively found, especially in animal substances; oxygen and hydrogen exist in almost all; but the element which is peculiarly organic, and which, with the one exception of ammonia, exists in all bodies derived from an animal or vegetable source, is *Carbon*. It is hence that I have deferred the description of carbon and its compounds until I could pass directly from it to the great variety of organic bodies of which it is the basis. With the constituents of inorganic bodies it has but an accidental connexion; for, as I shall hereafter show, there is no form of

carbon which has not at some time made part of an organized being. Besides these six elements of organic bodies, there are many which enter into the structure of animals and plants, and are subservient in an important degree to the proper performance of their functions, without being really constituents of their organic tissues or secretory products. Thus iodine and bromine exist in many marine plants and sponges; common salt and oxygen salts of potash, soda, lime, and magnesia exist in most animal and vegetable juices; phosphate of lime constitutes the bony skeleton of one, and carbonate of lime the testaceous covering of another tribe of animals, while silica forms the solid basis of some of the lower tribes of zoophytes. In the red colouring matter of the blood, iron is an essential element, and the same metal has been found in minute quantity in other parts of animals; indications of fluorine and of silica have been found in the bones and teeth; but in all these instances, except the one fact of the iron element of red blood, we find these saline substances to be contained in fluids in a condition of mere physical solution, or to be deposited as solids in the bones or teeth in a purely inorganic form, clearly to be distinguished from the proper state of organic combination, in which the carbon, hydrogen, oxygen, and nitrogen of the tissues and secretory products are united.

Among organic bodies, it is necessary to distinguish three classes, which differ no less in complexity of composition than in the circumstances under which they are formed, and their relation to organic bodies. These are, first, those bodies which are directly elements of an organized and living being, and which, while in connexion with it, appear to possess the power of elaborating, from certain nutritious juices, additional material similar to themselves. Such are the organic constituents of the animal and vegetable tissues and of the blood, which, while in connexion with, and forming portions of the animal or plant, participate to a certain degree in its vitality, and do not obey the laws of ordinary affinity, unless by being, in the first instance, killed; these bodies should be more properly called *organized* than merely *organic;* their chemical relations commence only when they have been deprived of their most essential character, *life.* They are organs; their constitution cannot be expressed in formulæ, nor their properties accounted for by analysis. After their death we may obtain from them, by chemical treatment, a variety of organic bodies; but that they were composed of these bodies, and that their properties resulted from the combination of such elements as we extract from them, it would be false philosophy to imagine. The fibrine and albumen of the blood, the muscles, and the cellular tissues, the fatty matter of the brain, perform their functions in virtue of vital power, and not of any chemical properties they possess. The albumen of the egg is not a chemical substance, but a delicately-constructed mass, destined to be transmuted into the organs of the chick, and by participating in its life, protected from putrefaction. But when albumen is precipitated by corrosive sublimate, it is killed, and the product of its decomposition combines with the oxide of mercury.

This class of bodies have their origin, therefore, in actions purely

vital. They have a structure organic-molecular, totally different from crystallization, and for the most part consisting of minute cells. When dead, these tissues undergo spontaneous decomposition, with more or less rapidity, according as their composition is more complex; but for this water must be present. Some forms of animal tissue, which appear to lose the organized structure and vitality with which they were at first formed, are capable still of remaining in connexion with the living system, and, although dead, have no tendency to putrefy, probably from not being in any degree soluble in water. The formation and growth of nails and hoofs, hair and horns, are examples of the important uses of this property.

It is by virtue of the vital forces of the bodies of this first class, not individually, but united together so as to constitute the tissues, glands, &c., of plants and animals, that the organic bodies of the second class have their origin. These are substances produced (secreted) from the elements by which organized bodies are nourished, probably by the union, under peculiar conditions, of such portions of the constituents of the food as were not proper or proportioned to be assimilated to the organized tissues of the living being itself. It is thus that, by a plant which uses water, carbonic acid, and atmospheric air as nutriment, after the assimilation of a certain quantity of their constituents to its proper tissues, sugar, starch, and albumen, adapted for the nutrition of its young, may be formed as secreted products, and oils, resins, colouring matters, &c., rejected as useless or injurious.

The third class of organic bodies contains those which are evolved by the chemical decompositions, whether spontaneous or artificial, to which substances of the first and second class are subjected. Thus sugar, by fermentation, yields alcohol and carbonic acid; alcohol, by oxidation, yields acetic acid, or aldehyd; acetic acid, variously treated, produces acetone, or alkarsin; while ligneous fibre gives origin, when heated, to a crowd of organic products, of which pyroxylic spirit is an example.

It is very interesting to contrast these classes of bodies with each other, in relation to the forces by which their constitution is regulated, as compared with the simpler forms of affinity by which the actions of inorganic elements are controlled. In the first there is found nothing referrible to chemical attraction; all affinity is annulled by the supremacy of life and organization. Hence it is only when dead that such bodies can be analyzed, and by treatment with reagents a crowd of products belonging to the third class be obtained from their more or less evident decomposition. No matter, therefore, how perfect our mediate or immediate analyses of such substances may be, the synthesis of such bodies, or their production by the union of their elements, is strictly impossible to the chemist. The formation of a molecule of albumen would not be a case of chemical combination, but of the formation of a portion of an organized cell; it would require not merely the combination of its elements, but also that the compound should have *life* imparted to it.

In relation, however, to the second and third classes, the circumstances are quite different; although we cannot trace, precisely,

the force by which the organized tissues act in eliminating from a liquid of uniform composition, such as the blood or sap, the various secretions which constitute the second class, yet the circumstances of their formation admit of being examined, and already some insight has been obtained as to the way in which organic bodies may separate, or be converted into others, without reference to the mere affinities of their elements, by means of the influence that has been already described as *catalytic* (p. 236, *et seq.*); in this way the functions of organized tissues may be imitated, and a true synthesis of organic bodies of the second class may be effected. With the bodies of the third class we find, also, that the circumstances of their formation are either purely artificial, or capable of being easily imitated, and the reactions by which they are evolved, although often catalytic, fall, in the majority of cases, under the rules of ordinary affinity. In structure, also, the bodies of the second and third class range themselves with inorganic compounds; those which are solid may, for the most part, be obtained crystallized, and the liquid substances possess definite freezing and boiling points.

Between such organic bodies and mineral substances we find the greatest similarity, not merely in their physical relations, but in chemical properties also. The great classes of acids and bases exist, well marked, among organic bodies, and in their combinations with each other, the same principles of multiple and equivalent combination are followed as hold for inorganic compounds. So perfect is the analogy of general characters, that it has long been an object with chemists to unite, under one principle, the laws of composition of organic and inorganic bodies; and as the characteristic distinction of mineral substances is to consist of a series of elements which are respectively combined, two and two, in virtue of their opposite affinities, attempts have been made to reduce the complex constitution of organic bodies to the same principle of binary union, by supposing that certain of the elements are, in the first instance, grouped together so as to form a single molecule, and that this, acting as a simple body, combines with the element which remains. It is from the discovery of cyanogen, and the discussions as to the nature of the ethers and of the ammoniacal salts, that we must date the positive introduction of this theory of compound radicals into chemistry. Its utility has not been limited to the explanation of the constitution of organic bodies; on the contrary, it has been applied successfully to explain the phenomena presented by numerous classes of inorganic compounds, such as the compounds of sulphur and oxygen, noticed p. 292, and especially to the foundation of the binary theory of salts, as described in the fifteenth chapter.

Were we, however, to apply the theory of compound radicals indiscriminately to explain the constitution of organic bodies, we should be liable to fall into continual error. The criterion which I would assume as decisive of the constitution of an organic body is, whether certain of its elements may be exchanged for others, in accordance with the ordinary laws of substitution of inorganic bodies, and thus a series of compounds be produced, through which some elements of the original substance shall have passed untouched,

and from which again, by suitable reactions, the original substance can be obtained unaltered. In such case I would consider those elements which remain unaffected as being strictly united with each other, and constituting a compound radical, which, combining with other bodies, gives origin to a series of compounds more or less extensive. Thus, if we treat oil of bitter almonds, $C_{14}H_6O_2$, by chlorine, we obtain a compound $C_{14}H_5O_2Cl.$, which gives, with iodide or sulphuret of potassium, bodies whose formulæ are respectively $C_{14}H_5O_2$ I. and $C_{14}H_5O_2S$. Again acted on by oxygen, it gives crystallized benzoic acid, $C_{14}H_6O_4$, or, rather, $C_{14}H_5O_3+Aq$. Now it will be seen that, throughout this whole series, the element $C_{14}H_5O_2$ has remained unaltered. In the oil it was combined with hydrogen; in benzoic acid it unites with oxygen; in the other bodies it is united with chlorine, iodine, &c., and from these the oil may be recovered by processes by no means indirect. Now when we state that in these compounds the elements $C_{14}H_5O_2$ are united, first with each other, by an affinity which ordinary reagents cannot overcome, and that this compound group unites with the simple bodies, hydrogen, oxygen, &c., by an affinity so much weaker that they can be readily substituted for each other, we state only an established fact, and in denominating the group, $C_{14}H_5O_2$, the root or radical of the series of bodies thus produced, we involve no hypothetical idea. For brevity, we express that compound radical by the symbol Bz., and we term it *Benzyle;* we write the formula of its combinations, respectively, Bz. H., Bz.Cl., Bz.I., and Bz.O.+Aq.

But we must not be induced, by the brilliancy shed on certain branches of organic chemistry through the application of this principle, to transgress the boundaries of sound induction. There are numerous organic compounds in which I believe that no binary structure exists, and, consequently, to which the theory of organic radicals should not be applied. It is the class of bodies characterized by a remarkable indifference to combination, and which, when decomposed by the influence of reagents, lose not merely one constituent and gain another in its place, but are totally transformed into new compounds, into which all of their original components enter, and towards which the reagent that had been applied frequently appears indifferent, so that the action appears to have more the character of catalysis than of true chemical affinity. Such bodies are gum, sugar, starch, some of the oily and colouring matters, urea, and many others: treat these bodies as you will, there are no phenomena of true replacement; they may be decomposed, but bodies of a totally different type are formed, and the original substances cannot be regenerated.

The organic radical which is thus assumed as the basis of a series of compounds, acts as a simple body, but it does so only in relation to the nature and intensity of the forces that act upon it; it may be decomposed, and frequently it cannot be separated from combination without total decomposition; hence few compound radicals can be isolated. But they can be decomposed, even while still in combination, by the intervention of powerful affinities; and this decomposition may be either total, so as to leave no trace of the original constitution of the substance, or by giving origin to

another series of combinations, may indicate a still more intimate constitution, and unveil an organic radical of a simpler structure acting as the basis of the first.

Thus we have seen what positive grounds there are for admitting benzyle, $C_{14}H_5O_2$, to be the radical of the oil of bitter almonds and of benzoic acid; but if we digest oil of bitter almonds with ammonia, all oxygen is removed, and we obtain a compound of nitrogen with the body, $C_{14}H_5$, which may also be obtained in other forms of combination. Now this organic substance, $C_{14}H_5$, acts as the basis of benzyle, for the oil of bitter almonds can be reproduced from it; and we thus obtain evidence of three stages of constitution in benzoic acid, whose formula should be written, therefore, as $(C_{14}H_5+O_2)+O$. The considerations described in p. 291 point out a perfect analogy to this in the constitution of sulphuric acid. Reduced to its ultimate elements, its formula is $S.O_3$; but powerful evidence shows that its real basis is sulphurous acid, and not sulphur, its rational formula being $S.O_2+O$. Now here the primary radical, $C_{14}H_5$, corresponds to sulphur, and benzyle to sulphurous acid; the total quantity of oxygen in such acids being divided into two portions, differing in order and intensity of combination with the ultimate radical. If we add to these considerations the view of salt-radicals, and consider the salts of benzoic acid as expressed by the formula $Bz.O_2+M.$, as that of the sulphates has been shown to be $S.O_2 . O_2+M.$, we observe even a fourth degree to which the molecular structure of the complex organic radical may be traced.

It is, indeed, when applied to explain the constitution of the organic acids, that the theory of compound radicals, as employed in the new views of the constitution of oxygen salts, appears most interesting, as the anomalies of properties and composition presented by the salts of the organic acids were more numerous and more extraordinary than any which the mineral acids presented, and were, indeed, totally unintelligible, until illustrated by the conjoined investigations of Dumas and of Liebig. An example of this may easily be selected. Of the organic acids, the majority are monobasic, but there are also many bibasic and tribasic; thus the citric acid, whose formula is $C_{12}H_5O_{11}$, combines with three atoms of base; the meconic acid, $C_{14}H.O_{11}$, is also tribasic; the tartaric acid, $C_8H_4O_{10}$, and the mucic acid, $C_{12}H_8O_{14}$, are bibasic. In these instances, the quality of combining with many atoms of base, which is so anomalous on the older view, necessarily follows from the formulæ of the hydrated acids, which become respectively, for citric acid, $C_{12}H_5O_{14}+H_3$; for meconic acid, $C_{14}H.O_{14}+H_3$; for tartaric acid, $C_8H_4O_{12}+H_2$; and for mucic acid, $C_{12}H_8O_{16}+H_2$. By its means many other singular properties of organic acids are explained: thus there appear to exist three acids, having absolutely the same composition of $C_2N.O.$, viz., the cyanic, the fulminic, and the cyanuric acids; they are isomeric; they possess excessively different properties. Whence has that difference its rise? If we say that the cyanic acid contains cyanogen ready formed, and that the others do not, it still remains to explain the isomerism of the others; and we find that the cyanic and cyanuric acids are transformed into each other by the slightest causes. We obtain, however, at once the key to this isomerism,

when we study the salts formed by these acids. The cyanic acid is monobasic; its hydrate is $C_2N.O.+H.O.$: the fulminic acid is bibasic; its hydrate is $C_4N_2O_2+2H.O.$: the cyanuric acid is tribasic; its formula is $C_6N_3O_3+3H.O.$ These acids are thus found to have different atomic weights; their molecular groups are ascertained to contain different numbers of molecules, and hence to admit of totally distinct internal structure. When expressed in formulæ on the binary theory, we have $C_2N.O_2+H.$ for the cyanic, $C_4N_2O_4+H_2$ for the fulminic, and $C_6N_3O_6+H_3$ for the cyanuric acid; and not merely the difference in nature of the acids, but also the distinctive characters of their salts necessarily result.

Although chemists are unanimous in regarding the principle of compound radicals as the basis of the philosophy of organic chemistry, yet science has not yet arrived at the point when the principle is adopted by all in the same form of detailed application. On the contrary, there are few specific examples of that principle that are not still open to discussion. The views of Berzelius on this subject are specially of importance. He considers that the compound radicals of organic bodies consist only of carbon and hydrogen, or of carbon and nitrogen: that they never contain oxygen. Hence he does not admit the existence of benzyle in benzoic acid or in oil of bitter almonds; he considers the only radical to be the carbohydrogen, $C_{14}H_5$, and benzoic acid to be directly $C_{14}H_5+O_3$. He looks upon the oil of bitter almonds as containing ready-formed benzoic acid, combined with the true hydruret of the radical, as $3(C_{14}H_6O_2)=2(C_{14}H_5+O_3)+(C_{14}H_5+H_3)$. The chloride of benzyle he looks upon as an oxychloride, $3(C_{14}H_5.O_2Cl.)$ being equal to $2(C_{14}H_5+O_3)+(C_{14}H_5+Cl_3)$. This is evidently the same difference of view that exists as to the nature of the sulphurous acid compounds, which Berzelius also regards as more complex. Thus the chlorosulphurous acid is, according to him, a compound of sulphuric acid with a terchloride of sulphur, $3(S.O_2Cl.)=2S.O_3+S.Cl_3$; and so in all other bodies similarly circumstanced.

The opinions of a man to whose extraordinary industry and genius we owe some of the most important additions, both theoretical and practical, that science has received since the epoch of Lavoisier, should not be rejected without much consideration; but on applying those ideas to express the constitution of the crowd of bodies, containing four or five elements, which have recently been discovered, we are led to suppositions destitute of experimental proof, and yet which, assuming the existence of numerous hypothetic bodies of anomalous constitution, and combined in very unusual ways, would require for their legitimate admission into science a very strong body of experimental evidence. It would be impossible here to discuss the principles of his opinion in detail; I am led to conclude, from the consideration of the whole body of facts which bear upon it, that it is inferior in power, and simplicity of explanation of known facts, and as an instrument of discovery, to the simpler view of the constitution of organic bodies which has been described; and being thus deficient in all the important duties of a sound theory, I do not hesitate to reject it.

The proposition of the theory of types by Dumas (see p. 234)

will probably constitute an epoch in science, by fixing attention on the permanent equivalency of an organic atom, notwithstanding complete alteration in the nature of its elements. This did not follow necessarily from the theory of compound radicals, nor does the conservation of the type require that the radical be preserved unaltered, but only the type of the radical. Thus, when aldehyd is changed into chloral ($C_4H_4O_2$ into $C_4H..Cl_3O_2$), the type is preserved, since the hydrogen is replaced by an equivalent of chlorine; the radical is altered, since acetyl, C_4H_3, is changed into C_4Cl_3, but the new radical is still constructed on the type of the original. The theory of types, so far from being inconsistent with the theory of compound radicals, is in perfect harmony with it, at least as I understand it, and as I believe it to have been proposed by Dumas The bases upon which it rests may be announced as follows:

1st. That the hydrogen of a compound radical may be replaced by chlorine or by oxygen, &c, equivalent for equivalent, and a new radical thus produced, which, being constructed on the same type as the original, will have the same general laws of combination, and will hence form compounds of the same type as those containing the original radical. Thus, from C_4H_3 may be formed C_4Cl_3, and these, combining with oxygen and water, form $C_4H_3O.+Aq.$ or $C_4H_3O_3+Aq.$, and $C_4Cl_3O.+Aq.$ or $C_4Cl_3O_3+Aq.$: also, by uniting with chlorine, they produce $C_4H_3Cl.$ and $C_4Cl_3Cl.$

2d. That when bodies of the same type, and containing radicals of the same type, are subjected to the action of strong affinities, by which their constitution is broken up, the resulting products are constituted also upon the same plan, although differing in composition; thus $C_4H_4O_4$, when heated with potash, gives $2C.O_2$ and C_2H_4; and $C_4H..Cl_3O_4$, similarly treated, gives $2C.O_2$ and $C_2H.Cl_3$; the types of $C_2H.H_3$ and $C_2H.Cl_3$ being the same, and containing equivalent radicals.

3d. When bodies of the same chemical, though of different mechanical types, or, as I would term them, bodies of the same natural families, as the alcohols, are submitted to the action of affinities of equal power, the bodies generated have the same relation to one another as the original bodies had; and the radicals are either unchanged, or all changed in a similar degree. Thus from wine alcohol ($C_4H_6O_2$), methylic alcohol ($C_2H_4O_2$), essential oil of potato spirit, $C_{10}H_{12}O_2$, and ethal, $C_{32}H_{34}O_2$, there are produced by the action of potash a series of acids, each having the same type and containing the same radical as its alcohol; thus the acetic acid ($C_4H_4O_4$), the formic acid ($C_2H_2O_4$), the valerianic acid ($C_{10}H_{10}O_4$), and the ethalic acid, $C_{32}H_{32}O_4$.

Considered in this way, the theory of types is an important addition to our ideas on the constitution of organic bodies. It serves to attach, under a few very simple principles, numerous classes of compounds, whose composition would otherwise appear very complex and anomalous, and will probably, when applied to the study of such bodies as, not containing compound radicals, give only their molecular group as a mass to our examination, become a source of still more important additions to our knowledge.

Although each organic substance gives, when acted on by re-

agents, products which are characteristic of, and often peculiar to itself, yet there are some general rules which, being now noticed, will obviate the necessity of much detail hereafter.

When an organic substance is treated with dry chlorine, it either combines directly with the gas, or, as more frequently happens, hydrogen is removed to an amount equivalent to that of the chlorine absorbed. Even in the first case, the direct union is often but apparent, and arises from the muriatic acid formed combining with the true product. Thus olefiant gas, C_4H_4, gives the oily liquid $C_4H_4Cl_2$; but this, in place of being a direct combination, consists of $C_4H_3Cl.$, which is the true product formed by substitution of Cl. for H., but is united with the H.Cl. thus generated.

If water be present, it influences the reaction very much, being generally decomposed. In some cases, all the chlorine unites with its hydrogen, while the oxygen combines with the organic substance; but, generally, the chlorine unites with both elements of the water, forming muriatic acid, which remains free, and hypochlorous or chlorous acids, which enter into the composition of the organic product. In other cases, again, the presence of water does not appear to exercise any influence.

When an organic substance is treated with nitric acid, it is always raised to a higher degree of oxidation. Very rarely does the action stop there. Hydrogen is usually separated, and oxygen put in its place; while the new products formed contain usually a smaller number of molecules than the original organic substance. Thus gum ($C_{12}H_{10}O_{10}$), when acted on by nitric acid, gives, first, by simple oxidation, mucic acid ($C_{12}H_{10}O_{16}$); but, if the action of the acid be more violent, all hydrogen is removed, and two atoms of oxygen substituted, thus producing $C_{12}O_{18}$, the elements of six atoms of oxalic acid.

In many cases, the action of nitric acid is not limited to the oxidation, whether direct or indirect, of the organic substances; but, by the removal of some hydrogen from it, in combination with some of the oxygen of the nitric acid, water is formed, and the nitrogen, or nitric oxide, or nitrous acid, combines with the remaining organic elements, and forms new products. Thus, from napthaline and benzine, numerous substances containing nitrogen are derived. This fixation of nitrogen may occur even with bodies which already contain it; thus indigo, treated with nitric acid, produces bodies, the indigotic and the picric acids, which contain a larger proportion of nitrogen than the indigo itself.

The peroxides of manganese and lead often serve to oxidize organic bodies in a more regulated manner than nitric acid, the new substance combining with the protoxide of the metal; thus, by PbO_2, uric acid is decomposed into allantoin, urea, and oxalic acid.

By fusion with hydrate of potash, the oxidizement of organic substances is very powerfully effected; water being decomposed, its hydrogen evolved, and the oxygen uniting with the organic body to form an acid, which remains combined with the potash. Thus alcohol, $C_4H_6O_2$ and $2H.O.$, produce acetic acid, $C_4H_4O_4$, and H_4 becomes free. Often the organic substance is merely broken up into other bodies of simpler constitution, as when tartaric acid, $C_8H_4O_{10}$,

by fusion with potash, is decomposed into acetic acid, $C_4H_4O_4$, and oxalic acid, $2(C_2O_3)$. In every case, if the temperature be much raised, carbonic acid is one of the products; thus acetic acid ($C_4H_4O_4$) separates into C_4H_4 and $2C.O_2$.

The action of sulphuric acid on organic bodies may be very different, according to circumstances; thus from starch we may obtain, by a merely catalytic influence, gum, grape-sugar, and ultimately sacchulmine. In these cases, the sulphuric acid remains totally unchanged and free, but generally it enters into combination with the organic body, either without decomposition, as in the sulphovinic and sulphomethylic acids, or else water is formed by its reaction on the organic body, which, thus deprived of an atom of hydrogen, combines with hyposulphuric acid, S_2O_5. It is thus that the sulphurous element exists in the sulphobenzoic acid, the isethionic acids, &c.

If an organic substance containing nitrogen be acted on by these reagents at a high temperature, this is generally separated under the form of ammonia; water being decomposed, and its hydrogen so applied, while its oxygen forms the ordinary oxidized organic products. If potash be the reagent, the ammonia is expelled, and a salt of potash with the new organic acid remains; if sulphuric acid be the reagent, the organic acid is set free, and a sulphate of ammonia remains.

By the action of heat upon fixed organic compounds, a variety of products are formed, which may generally be described as formed by the abstraction of a portion of carbon and oxygen, as carbonic acid, and of hydrogen and oxygen, as water. Hence such pyrogenic products are always richer in hydrogen and carbon than the bodies they are formed from, and of less acid characters. This kind of decomposition will, however, require to be described in a distinct chapter.

CHAPTER XVII.

OF CARBON, AND ITS COMPOUNDS WITH OXYGEN, SULPHUR, AND CHLORINE.

Carbon exists in large quantities, and very extensively distributed in nature, as a constituent of all vegetable and animal bodies. It is found, also, in the mineral kingdom, under forms, however, which may be shown to have originally been derived from organic bodies. Thus the different varieties of coal have been produced by the aggregation of great quantities of wood, the materials of primeval forests, which, being submerged in water, and covered by the gradually-deposited layers of sand and mud, have been elevated, in connexion with the strata of clay and sandstone so produced, to their present situations. The wood thus circumstanced has undergone a kind of decomposition, which shall be hereafter fully noticed, and the mixture of fixed and volatile organic products, which constitute our

coal, has thus its origin. This formation of coal, as well as the formation of peat and turf at the present day, almost at the surface, is accompanied by a disengagement of carbonic acid in large quantity, and hence the probable source, in the air and in mineral waters, of that substance, of which, also, much may be derived from the respiration of animals.

A more strictly mineral form of carbon is that of carbonic acid united to lime, and to other metallic oxides, forming the numerous class of native carbonates. Of these the most abundant is the carbonate of lime, which, under the form of chalk, oolite, coral, mountain limestone, &c., constitutes a large proportion of the geological formations of our globe. In all these cases, the rock is formed of shells of animals, aggregated together in great masses; these geological formations, resulting from the collection, at the bottom of a sea or lake, of the spoils of myriads of generations of those animals, which, by superincumbent pressure, may be more or less densely aggregated; or by proximity of igneous rocks, may be partially or completely fused, and their organic characters obliterated to a greater or less degree. In this way the crystalline marbles are formed, in which few or no traces of organic origin remain. The comparatively small quantity of carbonate of lime, which is found separately and distinctly crystalline, either as arragonite or calc spar, may be traced to the solvent action of water impregnated with carbonic acid, filtering through strata containing shells, and then gradually depositing, in favourable situations, the matter it had thus taken up, in crystals, the form of which depends upon the temperature at which they are produced (page 225). The other native carbonates, of which the quantity is very small in comparison with that of the carbonate of lime, may have been produced by double decomposition. Thus a water, holding carbonate of lime in solution, filtering across a stratum containing oxidized iron or copper pyrites, would give origin on the spot to a crystalline deposite of sulphate of lime, and, at a certain distance, carbonate of iron or of copper would be separated. Those instances suffice to point out the reasons for considering carbon as truly the organic element, and that its appearance in a mineralized condition arises from secondary actions.

Carbon presents itself in a great variety of forms. Absolutely pure, it constitutes the diamond, which, from its exceeding hardness, brilliancy, and rarity, ranks as the first of gems. It is found disseminated in alluvial strata in Golconda, Brazil, &c., and is separated from the sand and mud by processes of washing. No deposition of diamond in rocks has ever yet been found. It crystallizes in forms of the regular system, generally having a great number of sides, bounded by curved edges, in virtue of which it splits glass like a wedge, in place of scratching it as a file. Its crystals are generally hemihedral, and frequently rough and discoloured at the surface. These crystals all cleave parallel to the faces of a regular octohedron (fig. *f*, p. 26), but the properties of the diamond separate it completely from the proper mineral crystals of the regular system. Thus it possesses double refraction in some cases; it polarizes light elliptically; its structure has been found by Brewster to consist in layers, sometimes containing cavities, indicating that the crystal had

been originally soft, and only concreted by degrees; and in the recent researches of Dumas on the atomic weight of carbon, it was found that, when burned, diamonds generally leave behind a minute skeleton of inorganic matter. These considerations fully show that the diamond derives its origin from the decomposition of organic matter. The diamond is the hardest body known; it cuts every other, and can be ground only by means of its own powder. It is usually colourless, but sometimes brown or rose-coloured; its refractive power is very great (2·439), whence its great brilliancy. It conducts heat and electricity very badly; it resists most chemical agents, but burns in melted nitre brilliantly, forming carbonate of potash; it burns, also, when heated to redness in oxygen gas, and evolves sufficient heat to maintain the continuance of the combustion; its specific gravity is about 3·5.

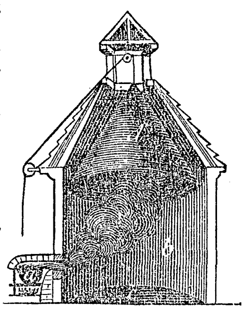
Another very remarkable form of carbon is that of *plumbago* or *graphite*. This is found in many localities, but sufficiently pure for the purposes of the arts only in Borrodale, in Cumberland. It is perfectly opaque, crystallized in rhombohedrons, or six-sided tables; but its usual appearance is in brilliant leaves or spangles; it is soft and unctuous to the touch, and gives, on paper, a continuous gray streak, whence its name of *blacklead*, and its use in making pencils. Its formation appears to be connected with the action of iron, and with a high temperature: it is found only in igneous rocks, as granite and mica slate, and contains almost always a large quantity of iron intermixed in the metallic state, so that it was once supposed to be a carburet of iron. Graphite may be formed artificially by adding charcoal to melted cast iron; the charcoal dissolves largely, but on cooling is found to separate in brilliant flexible plates, more or less regularly six-sided. Graphite is lighter than diamond, its specific gravity being 2·5, and it conducts heat and electricity much better. It is very hard to set on fire, and does not continue to burn unless heat be applied from without.

Carbon, in a form more or less mixed with foreign matters, is obtained by the application of a very high temperature to animal or vegetable substances in close vessels. The kinds of carbon thus produced still differ very much. Thus *coke* is obtained by heating coal in iron retorts until all the volatile products are driven off, and the excess of carbon remains mixed with the earthy matter which all coal contains. The properties of coke approximate more or less to those of graphite, according to the temperature at which it has been produced. By the proximity of igneous rocks to coal under the earth, a similar expulsion of its volatile matters may be effected, and a form of carbon nearly pure, *anthracite*, results. These fuels are difficult to light, but, when once ignited, give out an intense heat by their combustion.

If an organic substance, which contains hydrogen and carbon, be set on fire, and there be a copious supply of air, it is totally converted into water and carbonic acid; but if the supply of air be limited, the affinity of the hydrogen for the oxygen preponderates, and no carbon is consumed until all hydrogen is converted into water. By this method of imperfect combustion, several forms of carbon are prepared, such as wood-charcoal and lampblack. If we

take a splinter of wood and set it on fire, we observe that at first only the volatile products of the wood burn with flame, and that a mass of charcoal forms inside, and remains unaltered as long as, being surrounded by flame, it is protected from the air; but when the end projects beyond the flame, it ignites and burns away, leaving only a trifling ash. If, however, a tube be taken, and, as in the figure, as the combustion advances along the stick *b*, the burned portion *a* be gradually plunged into a narrow tube, this becomes filled with carbonic acid, which does not support combustion, and the cylinder of charcoal formed may thus be permanently preserved; on this principle *wood-charcoal* is prepared. Billets of wood are heaped together regularly, so as to form a hemispherical mass of about forty feet diameter; in the centre a hole reaches from the top to the bottom, forming a chimney. The outside is then coated with sods, so as to render it impervious to air except at the bottom, where some apertures are left. Burning charcoal is then thrown into the chimney, and the fire communicating to the billets, these burn with a supply of air so limited that the charcoal remains unconsumed, the combustion commencing at the top and proceeding down. The outside of the heap is then covered with denser sods, so as to cut off the supply of air as the combustion proceeds. When the carbonization has been completed, the whole mass is covered up and allowed to cool perfectly before being opened. In this country, most of the charcoal used is obtained in the preparation of vinegar by the destructive distillation of wood, as will be hereafter noticed. The quantity of charcoal produced from wood varies very much with the rapidity of the process; the generality of fresh woods yielding but thirteen or fourteen per cent. by a rapid decomposition, while, when slowly charred, they may yield twenty-five or twenty-six. The mode of conducting the process, therefore, must be changed according as the residual charcoal, or the volatile materials, are the most valuable products. The charcoal preserves, in a remarkable manner, the structure of the wood from which it is produced, so that by the microscope some of the most delicate forms of vegetable organization may be traced in charcoal that has been slowly prepared.

Lampblack is formed by a still more direct application of the principle of imperfect combustion. In the apparatus represented in the figure, *a* is a pot placed in a furnace which is vaulted over, so that all vapour from it may pass into the chamber *b*, *c*, while by some apertures a small quantity of air is allowed to sweep over its surface; the sides of the round chamber are lined with leather, and above is a conical cover of coarse linen, *d*, through which the draught from the furnace passes, and which may be lowered or raised by the cord and pulley. A quantity of pitch or tar is placed in the pot and made to boil; it takes fire, and, as the quantity of air which has access to it is very small, the hydrogen alone burns, and the carbon, being carried up by the current in a very finely-divided state, is deposited on the sides and cover as an impalpable powder.



Animal charcoal is produced by the decomposition of animal matters in close vessels. From its properties, which I shall just now notice, it is manufactured

in large quantities for the arts, especially from bones, and is hence called *Ivory-black* or *Bone-black*. The bones are placed in iron cylinders, which are arranged, vertically or horizontally, in a furnace, in connexion with a series of condensing vessels containing water; the volatile constituents of the animal matter being expelled principally as carbonate of ammonia, of which a large quantity is thus made, the excess of carbon remains in a state of very minute division, mixed with the earth of bones (phosphate of lime).

Some of the most important uses of carbon are founded on properties which the various forms of it possess in different degrees. Its inflammability varies with its density and closeness of aggregation; being least in graphite, and becoming so great when wood charcoal, prepared at a low temperature, has been reduced to powder for the preparation of gunpowder, as to inflame sometimes spontaneously, and give rise to destructive accidents. Carbon possesses a remarkable tendency to unite with colouring and odorous substances. This property is specially possessed by ivory-black, in consequence of the extreme degree of division of its particles. When a purely organic body yields carbon, the molecules of the latter aggregate themselves to a degree which depends on the temperature; and if, as in wood, there be a fusible ash present, this acts as a cement, and diminishes the porosity very much. If the organic substance be fusible, as starch or sugar, the closeness of texture of the charcoal becomes still greater, and its utility less; but in bones, the molecules of organic matter are separated by an infusible earthy salt, and when carbonized, the charcoal is obtained in the greatest possible state of comminution. A still more efficient charcoal is formed by calcining dried blood, hoofs, or horns, with carbonate of potash, which prevents the aggregation of the particles of carbon, which, the alkaline salt being washed out with water, is left in the most active condition possible. In the arts, this property is applied to the purification of sugar; to clearing solutions of many organic substances; and barrels in which water is to be kept are charred on the insides, in order to remove any organic matter described in the water, which might be liable to putrefy.

The following table contains some numerical results of the relative decolorizing power of equal quantities of carbon in various forms; the first column containing the number expressing the power of removing the colour of a solution of indigo, and the second column that of a solution of coarse sugar. The power of ivory-black is taken as the standard:

Kinds of Charcoal.	Indigo.	Sugar.
Common ivory-black	1	1
Well ignited lampblack	4	$3\frac{1}{3}$
Lampblack ignited with pot ashes	17	10
Charcoal from the decomposition of acetate of potash	5·6	4·4
Starch ignited with pot ashes	11·9	8·9
Blood ignited with phosphate of lime	11·9	10
Ivory-black digested in muriatic acid	1·9	1·7
Ivory-black digested in muriatic acid, and afterward ignited with pot ashes	45·3	20
Blood ignited with pot ashes	50	20

The decolorizing power is thus not the same for all bodies. If charcoal that had once been used be again ignited, it does not recover its activity, as the colouring matter fuses before charring, and thereby lessens its porosity. Charcoal possesses also a remarkable power of absorbing gases. If a fragment of wood charcoal, which had been strongly heated, and allowed to cool without access of air, be introduced into a tube containing ammoniacal gas, in the mercurial pneumatic trough, an immediate absorption occurs, to the amount of ninety times the volume of the charcoal. In other cases the absorption is not so great; a cubic inch of boxwood char coal, which is the most active, absorbing

90 cubic inches of	ammonia.		40 cubic inches of	nitrous oxide	
85 " "	muriatic acid.		35 " "	carbonic acid.	
65 " "	sulphurous acid.		9·25 "	oxygen.	
55 " "	sulphuretted hydrogen.		7·5 "	nitrogen.	
35 " "	olefiant gas.		1·75 "	hydrogen.	

These gases in this absorption undergo no chemical change, but appear to be retained on the surface of the pores of the charcoal by powerful cohesion, and probably in the liquid form, as it is such gases as may be rendered liquid by pressure that are absorbed in larger quantity.

The number expressing the atomic weight of carbon is not at present exactly known. By Drs. Prout and Thompson it was fixed at seventy-five upon the oxygen, and six upon the hydrogen scale; but the investigations of Berzelius and Dulong induced the majority of chemists to adopt a higher number, 76·4 or 6·13. The latest experiments of Dumas and Stass directed to the determination of this point, induce those eminent chemists to recur to the original number, 75; while Liebig and Redtenbachar have deduced from their researches the numbers 75·8. Dr. Clarke, from a re-examination of Berzelius's results, finds that they give, when corrected for some minute sources of error, 75·6; and, until opinion becomes more unanimous upon this important point, I shall assume as the number expressing the equivalent of carbon, 75·6 upon the oxygen, and 6·05 upon the hydrogen scale.

If we admitted the truth of Dulong and Petit's law (p. 66, 219), connecting the specific heat with the atomic weights of bodies, we should consider the equivalent of carbon to be double that above given, as Regnault has found the specific heat to be 0·241. This idea appears favoured by the fact, that it is doubtful whether there really exists a combination of carbon containing an odd number of equivalents, taking the number as 6·05. But the force of this result is totally obviated by the fact that the specific heat of carbon varies with its state of aggregation so much, that for poplar charcoal it is 0·296, and for diamond but 0·147; hence we cannot connect these numbers with the chemical equivalent of the body.

Notwithstanding that carbon is absolutely infusible and fixed, yet, from the variety of gaseous and volatile compounds into which it enters, and whose constitution is remarkably illustrated by the application of the theory of volumes, *carbon vapour* is frequently spoken of by chemists, although its existence is purely hypothetical. I have mentioned (p. 215) the difference of opinion as to its specific

gravity, which I assume at 843. The new results would appear to show that it is really but 836·8 upon the one, or 418·4 upon the other view.

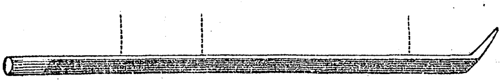
General Principles of Organic Analysis.

Substances which contain much carbon are, in general, easily recognised, by their being more or less combustible, and forming carbonic acid when burned, besides often leaving a carbonaceous residue. Even where the bodies are not inflammable simply, they deflagrate more or less violently when heated with nitre, and form carbonate of potash.

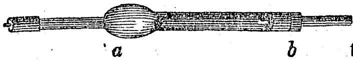
Although it is not within the scope of the present work to embrace the details of chemical analysis, it would yet be improper to omit a general description of the methods adopted for the determination of the quantities of carbon, hydrogen, and nitrogen, which enter into the constitution of organic bodies. The general principle upon which this process is carried out, consists in supplying oxygen so abundantly to the organic substance, as that all its carbon shall be converted into carbonic acid, and all its hydrogen into water, and yet the supply of oxygen shall be so graduated, and the decomposition so regularly progressive, as to admit of the products being collected with accuracy. The nitrogen is always determined by an independent operation, in which the other elements are neglected; and, although processes have been proposed which provided for a direct valuation of the oxygen, it is found in practice better to obtain its value by subtracting the weight of all the other constituents from that of the substance employed. For the analysis of an organic substance, there are, therefore, two processes; the first, to determine the carbon and hydrogen, and the second to determine the amount of nitrogen.

The substance generally used to supply oxygen is the black oxide of copper, prepared by gently igniting the nitrate. Sometimes chromate of lead is employed, particularly for bodies rich in chlorine. Where the substance to be analyzed burns with difficulty, it is often necessary, in order to be certain of the complete combustion of the carbon, to pass a stream of oxygen gas over it at the termination of the process.

A straight tube of hard Bohemian glass, of about sixteen inches long, and from one third to half an inch in diameter, is to be drawn out at one end to a point, which is to be sealed and turned up, as in the figure.



Some oxide of copper (or chromate of lead, as the case may be) is to be then poured in so as to occupy about two inches of the tube next the bottom. As much oxide of copper as will occupy about six inches of the tube is to be then intimately mixed with the substance to be analyzed, if it be solid, by rubbing in a mortar, and this mixture then introduced. The mortar is next to be rinsed out with as much oxide of copper as will fill two or three inches; and, finally, pure oxide of copper is to be placed for about three inches in front of all. The whole materials thus introduced will occupy about fourteen inches of the tube, when it is shaken down by tapping it, nearly horizontally on the edge of a table, so as to leave, as in the figure, where the dotted lines mark the spaces of the several portions, a free passage above the materials from end to end of the tube. In these operations the greatest care must be taken to avoid all access of moisture; the tube, the mortar, and the substance must be made absolutely dry, and the oxide of copper, being powerfully hygroscopic, should be ignited before each operation, and allowed to cool under a bell glass with a capsule of oil of vitriol, or by being placed while very hot in a long dry tube, which is then to be corked completely tight. After the substance and oxide of copper have been placed in the tube, it is generally necessary to remove even the traces of damp which might have been absorbed by exposure to the air during the mixing in the mortar. This is done by means of a small exhausting syringe, which is attached to the combustion tube by a cork, a tube containing fused chloride of calcium being interposed. The combustion tube is bedded in warm sand, and by means of the syringe, the damp air it contains is withdrawn, and replaced by air, which, passing over the chloride of calcium, becomes completely dry. After a few repetitions of this process, all moisture is removed, and the combustion tube is ready to be attached to the other parts of the apparatus.

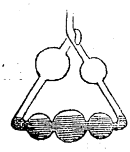


a *b*

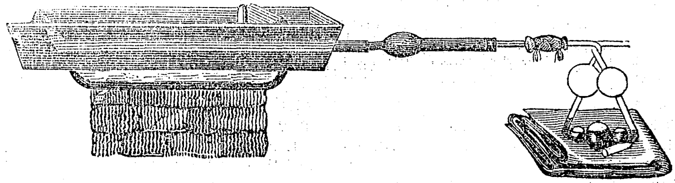
These are, 1st, a tube of the form represented in the figure, into which a little cotton wool is dropped at *a*, and it is then filled

with recently-fused chloride of calcium in fragments of the size of a split pea. At *b* a little cotton wool is also placed, and a small tube is connected with it by a cork. To its smaller end a cork is adapted, which accurately fits the end of the combustion tube, and which has been carefully dried. This apparatus (but without the last cork) is carefully weighed before the operation.

The second apparatus is the *potash bulb-tube*, the invention of which by Liebig was the great cause of the rapid progress of organic chemistry within the last few years, as it facilitated the analysis of organic bodies in a remarkable degree. It consists of a tube on which are blown five bulbs; the three interior communicating by pretty wide openings, but each outer bulb separated from the others by a couple of inches of tube. The proportions of the respective bulbs may be collected from the figure, which represents also the form into which the tube is bent. The three central bulbs are to be nearly filled with a strong solution of caustic potash (sp. gr. 1·25), and the apparatus attached to the small tube, *b*, of the *water tube* by a caoutchouc connector tied very carefully on. It is to be allowed to incline, at the angle represented in the next figure, so that the carbonic acid gas, when passing through it, shall bubble from bulb to bulb, without any danger of expelling any portion of the liquor.



The combustion tube is to be placed in a sheet iron furnace, the form and size of which may be collected from the figure, its open end so far projecting (1½ inches) as



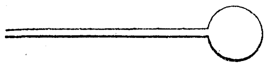
that the cork by which the water tube is attached shall not be in any danger of being charred, but yet shall be so hot that no water can condense upon it. The jointings being found to be completely tight, and the water tube and potash bulbs being attached, and arranged as in the figure, the analysis may be proceeded with. Some ignited charcoal is to be placed round the first three inches of the tube, and when the pure oxide of copper is completely red-hot, the next portion, which, having rinsed out the mortar, contains some traces of the organic substance, is to be similarly ignited. The hydrogen of the substance reduces the oxide of copper, and forms water, which is collected by the chloride of calcium in the water tube, and the carbon, also reducing the oxide of copper, is converted into carbonic acid, which, being dried in passing over the chloride of calcium, is totally absorbed by the potash in the bulbs. By the addition of burning charcoal, the combustion of the organic matter is made to progress down the tube, the operator being directed in his proceedings by the rate at which the evolution of carbonic acid and its absorption proceed, until he arrives within two inches of the end of the tube. He then stops until he has made the point and the pure oxide of copper near it red-hot, and then closes in the charcoal on the remaining space.

The combustion being thus completed, the tube remains, however, occupied by a mixture of watery vapour and carbonic acid, which must not be lost; for this the point of the tube serves. It is broken with a nippers, and then a current of air is gently sucked, by means of a tube fitted to the potash bulb-tube, through the whole apparatus; this carries the water vapour to the water tube, and the carbonic acid to the potash, so that all the products of the combustion are obtained. The apparatus is then taken asunder, and the potash tube and water tube weighed; the increase of weight gives, of course, the quantities of carbonic acid and of water collected, and hence, by simple calculation, the proportions of carbon and hydrogen contained in the quantity of substance that had been operated on.

If the substance had been one very difficult to burn, and hence requiring oxygen to finish its combustion, the tube is not drawn out at the end, but widened a little, so as to form a small bulb, in which some chlorate of potash is placed. At the end of the process, this being heated evolves oxygen, which not only burns any traces of carbon that might remain, but serves also to carry the carbonic acid and vapour fully into the water tube and bulbs.

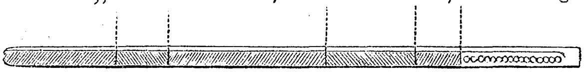
There are a variety of circumstances to be attended to in this operation, in order to obtain the high degree of accuracy which alone confers value on numerical results. These can be learned only in the laboratory, and not even from the most detailed de-

scription. My object is merely to afford an idea of the general principles of the method.



If the substance to be analyzed be liquid and volatile, it is introduced into small bulbs of the size of the figure, by the method given in page 11. There are generally two of these bulbs, one placed about two and the other about six inches from the sealed end of the tube, as shown in the figure; the little stem is broken across in the act of introducing them, so that the liquid may easily flow out, when, by the approach of a piece of red-hot charcoal, it is gently heated, so as to form a vapour. The peculiar precautions necessary in the management of the analysis of such bodies, and the methods adopted for non-volatile liquids and other bodies of peculiar properties, can only be learned by experience, and do not fall within my purpose to describe.

To determine the nitrogen of an organic substance, a long combustion tube is taken (2 or 2·5 feet), sealed at one end, but not drawn out, as in the figure. Next



the sealed end is placed carbonate of copper for a space of six or eight inches, and then the pure oxide of copper, the mixture, the rinsing of the mortar, and again pure oxide, occupying fourteen or fifteen inches, exactly as in the former case; in front of all, five or six inches are occupied by clean metallic copper in a finely-divided state, either as reduced by hydrogen from the oxide, or as very thin turnings. These divisions and the general form of the tube are given by the figure. To the combustion tube there is fitted by a tight cork a quill tube, which is in connexion on the one hand with an exhausting syringe, and then, by a vertical tube more than thirty inches long, passes to the mercurial pneumatic trough. All the joinings being found tight, and the combustion tube arranged in the furnace, red-hot charcoal is applied to the closed end of the tube, where it disengages carbonic acid from the carbonate of copper, which, sweeping through the apparatus, expels the atmospheric air. To render this the more effectual, the whole apparatus is exhausted by the syringe, and again filled with carbonic acid, and this is continued until the bubbles of gas which come over are perfectly absorbed by solution of potash. In this expulsion of the air of the apparatus, not more than one half of the carbonate of copper should have been used.

The fire is now to be withdrawn from the closed end of the tube, and applied to the part occupied by the metallic copper. When this is red hot, the combustion is carried backward, just as in the former example; and when all the substance has been burned, the coals are applied to the remaining carbonate of copper, which, evolving carbonic acid, clears out all the nitrogen of the apparatus, just as it had in the commencement cleared out all the atmospheric air. The mixed gases that are produced in this operation are received in a bell-glass which contains some strong solution of potash, by which the carbonic acid is absorbed, and the nitrogen remaining may then be measured. The volume of gas is next to be corrected for temperature and pressure, as directed in p. 57 and 20, and its weight then calculated.

The use of the metallic copper in the front of the mixture requires notice; when nitrogen passes over red-hot oxide of copper, there is always some nitric oxide formed, which would falsify the result, as its volume is double that of the nitrogen it contains; but nitric oxide is completely decomposed by red-hot metallic copper, pure nitrogen being evolved, and hence the purity of the resulting gas is secured by this arrangement. Indeed, in all combustions of an azotized body, the mixture should have some bright metallic copper in front of it.

The direct valuation of nitrogen is thus a very delicate operation, and occupies several hours. If the substance contain a large quantity of nitrogen, its amount may be indirectly ascertained in a much simpler way. The quantity of carbon in the substance is first learned by an ordinary analysis, then another combustion tube is arranged with very clean copper in front; but, in place of adapting the water tube and bulbs, the water is taken no count of, and the gases evolved are collected in narrow graduated tubes, over mercury. In order to clear out the air from the tube, some of the mixture next the sealed end is first ignited, and the gas allowed to escape, the tubes being filled from the products of the subsequent periods of combustion. In this case no weights need be attended to, as it is only the analysis of the gas in the tubes that is required for the result. The volume of gas in a tube being

marked, some solution of potash is introduced and agitated in it. The carbonic acid is absorbed, and the nitrogen remains, the volume of which is read off, taking care that the level of the mercury is the same inside as outside the tube. The relative volumes of the carbonic acid and nitrogen gases are thus found; and as an equal volume represents an atom for each, the relative number of atoms of carbon and nitrogen is thus determined; and as the total quantity of carbon is known by a previous experiment, the total quantity of nitrogen may be calculated. When the relation of the number of atoms of carbon to those of nitrogen is simple, as occurs in cyanogen and oxamide, $C_2N.$, mellon, C_3N_2, caffeine and taurine, $C_4N.$, this method gives very accurate results.

Where the organic substance contains chlorine, sulphur, arsenic, &c., it is to be destroyed by nitric acid, or by ignition with potash or lime, and the inorganic constituents then determined in the ordinary way. In organic salts the metallic basis is determined by igniting the substance, burning away the organic element, and determining the quantity of inorganic base by whatever method is best suited to its individual nature.

Carbon combines with oxygen in several proportions, of which three, those in which it forms the carbonic oxide, and the carbonic and oxalic acids, are the most important, and deserve the most detailed description.

Of Carbonic Acid. Eq. 275·6 or 22·05.

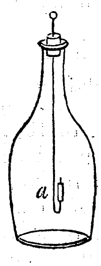
Carbonic acid exists in the atmosphere as a product of combustion and of the respiration of animals. Combined with metallic oxides, it forms the numerous class of native earthy and metallic carbonates, of which the carbonate of lime is much the most important. It is a result, also, of the slow decomposition of most vegetable substances, and is evolved in great quantity from the ground in volcanic countries. In the fermentation of sugar it is produced in abundance along with alcohol. For the purposes of the chemist, it is generally prepared by decomposing marble or calc spar by means of any stronger acid; from its cheapness, and the solubility of the residual salt, muriatic is generally employed. Some fragments of white marble being placed in a wide-necked bottle, the acid, diluted with its own volume of water, is poured in by a funnel tube, as in the figure, p. 247, and the gas which is evolved is conducted by the bent tube, to be made use of as required. The reaction consists in $H.Cl.$ and $Ca.O..C.O_2$ producing $H.O.$ and $Ca.Cl.$, which remains in the bottle, while $C.O_2$ is driven off. Carbonic acid being dissolved by water, and it being generally required in larger quantity than it is convenient to collect over mercury, we take advantage of the density of the gas to collect it in dry jars, as described and figured for chlorine in p. 301. The jar is known to be full when a lighted taper, applied near the mouth, is instantly extinguished.

The properties of carbonic acid are very remarkable; it is perfectly colourless and invisible; it is irrespirable, producing, when an attempt is made to breathe it, violent spasms of the glottis. If it be inspired, mixed with air, even in the proportion of 1 to 10, it gradually produces stupor and death, acting as a narcotic poison. Its specific gravity is 1·521. It hence, when disengaged in large quantities, whether by natural operations or in processes of manufacture, accumulates in all cavities within its reach, and may cause fatal accidents to animals who enter unadvisedly. Thus workmen

engaged in cleaning out dry wells or vaults, or the large vats from which fermenting liquors have been run off, should carefully observe whether a candle can remain for some time burning brightly at the bottom. In volcanic countries, caverns are frequently occupied to the level of their surface by this gas, exhaled from the ground ; and an experiment often tried, to amuse the traveller, consists in walking into such a cavern with a dog, which, holding the head near the floor, is almost instantly asphixiated by the layer of carbonic acid, while the men, whose heads are above its level, breathe pure air ; the dog, on being thrown immediately into a neighbouring pond, recovers from his stupor. Carbonic acid does not support combustion. A taper plunged into a jar full of the gas is instantly extinguished, and the high specific gravity of the gas may be well shown by placing a lighted taper at the bottom of a jar containing air, and taking in the hand another jar containing carbonic acid ; on inclining this jar, the heavy gas pours over the edge, nearly as water would do, into that in which the taper is placed, and, falling to the bottom, extinguishes it.

Water dissolves its own volume of carbonic acid gas, forming a solution of an agreeably acidulous taste, which sparkles when agitated ; it colours blue litmus paper of a wine-red, which disappears on exposure to the air or by heat. By means of pressure, water can be made to absorb a large quantity of carbonic acid, which escapes with effervescence when the pressure is removed, and is thus the basis of a variety of agreeable effervescing beverages. Solution of carbonic acid in water precipitates solutions of lime and barytes white, forming carbonates, which redissolve in an excess of the carbonic acid.

Under a pressure of thirty-six atmospheres, carbonic acid may be liquefied. It then forms a colourless, exceedingly mobile liquid, of specific gravity 0·83 at 32°, which is remarkable for its excessive expansibility by heat, it having four times that of air, or nearly one per cent. for each degree of Fahrenheit. When the pressure is suddenly removed from this liquid acid, it gasefies with such rapidity that, one portion absorbing heat from the other, this latter is rendered solid (see page 86). Solid carbonic acid can thus be obtained in large quantity by the apparatus contrived by Thilorier. It is a white body, in filamentous masses, like asbestus ; it evaporates but slowly ; it is very soluble in alcohol and ether ; the ethereal solution produces by its evaporation the most intense cold known, estimated at —180 degrees of Fahrenheit.



The composition of carbonic acid may be determined by very simple experiments. If into a bottle of pure oxygen gas we insert a little bit of charcoal, ignited at one point, at the end of the wire *a*, as in the figure, it burns with vivid scintillations, and the oxygen is all converted into carbonic acid. The stopper of the bottle, through which the wire passes, being perfectly tight, it will be found that the volume of the gas, when cold, has not sensibly altered, and thus that carbonic acid contains its own volume of oxygen. It consists, therefore, of

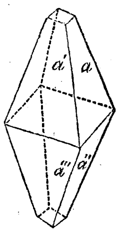
Two volumes of oxygen .	$1102 \cdot 6 \times 2 = 2205 \cdot 2$
One volume of carbon vapour	$843 \cdot 0$
Forming two volumes of carbonic acid	$2 \div \overline{3048 \cdot 2}$
Of which one volume weighs, therefore,	$= \overline{1524 \cdot 1}$

The corrected specific gravity of carbonic acid, 1·521, indicates that the theoretical density of carbon vapour should rather be taken as 836 than 843.

To demonstrate the existence of carbon in carbonic acid gas, it is sufficient to heat to dull redness, in a current of the gas, a small globule of potassium. The metal takes fire, burning with a brilliant violet flame, and forms potash, while carbon is abundantly deposited as a brilliant jet-black film on the interior of the tube.

Carbonic acid combines with the bases, forming a very important class of salts, the *carbonates*. It forms neutral, basic, and acid salts, which last are really double salts, containing carbonate of water, which, however, exists only in combination, as the carbonic acid does not combine with water directly in definite proportions. All salts of carbonic acid are known, by yielding, when acted on by muriatic acid in the cold, the gas possessing the properties now described.

Carbonate of Potash.—$K.O. . C.O_2$. Eq. 866·3 or 69·4. This salt, which is the great source of all other combinations of this alkali, is obtained for the purposes of commerce from the ashes of plants growing at a distance from the sea. The vegetable juices contain potash, combined with various acids, as the nitric, oxalic, acetic, malic, &c., which, by the burning of the wood, are converted into carbonates. The produce differs according to the kind of wood, and with the season. The softer and more juicy the plants are, the more potash they yield. Plants of the natural families compositæ and cruciferæ are the richest; the grasses rank next; and among the woods, the leaves yield more than the small branches, and these, again, more than the stems. In countries where there are large forests, as America and Russia, the small wood is burned, and the ashes collected; these are boiled with water in large iron pans or pots, from whence the name *potash* is derived. By this means, a large quantity of insoluble salts is separated, and the carbonate of potash, which dissolves, is obtained in a purer form by evaporation to dryness. It then constitutes the *pearlashes*, or refined potashes of commerce. Even these still retain much silica, sulphate of potash, and chloride of potassium, so that the best American pearlashes seldom contain more than eighty-five per cent., and Russian potash often not sixty per cent. of true carbonate of potash.

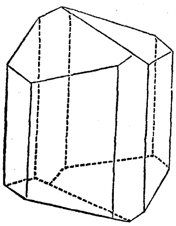


The purification of pearlashes being difficult, carbonate of potash is best prepared for chemical purposes by calcining cream of tartar; the tartaric acid which it contains is decomposed, and carbonic acid formed, which combines with the potash; the mass is digested with water, filtered to separate the excess of charcoal, and evaporated to dryness in a clean iron vessel. A white granular mass is obtained, the *salt of tartar* of the older pharmacopœias. It is very deliquescent, soluble in half its weight of water, and crystallizes with two atoms of water in

oblique rhombic octohedrons, a, a', a'', a''', as in the figure ($K.O.\ C.O_2 + 2\ Aq.$). It reacts strongly alkaline. It is almost insoluble in alcohol, and when added to weak spirit, combines with the excess of water, forming a heavy fluid, which remains separated from the lighter and stronger alcohol above.

As it is only the carbonate of potash that constitutes the value of pearlashes in the manufactures to which it is applied, it is important to be able to determine, by a single and simple operation, the relative worth of commercial samples. This process is termed *alkalimetry*. The best method of performing it will be described under the head of "Carbonate of Soda."

Bicarbonate of Potash, $K.O..C.O_2 + H.O..C.O_2$, is formed by passing a current of carbonic acid gas through a saturated solution of the neutral carbonate, the temperature of which should not be above 100°. On cooling, it crystallizes in right rhombic prisms of eight sides, as in the figure. It dissolves in four parts of cold water, and in much less when hot. If its solution be boiled, it abandons its second atom of carbonic acid, and becomes neutral carbonate. Its reaction on vegetable colours is feebly alkaline.

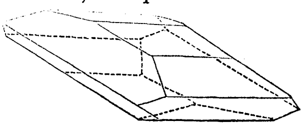


Carbonate of Soda—$Na.O..C.O_2 + 10\ Aq.$; Eq. $667{\cdot}3 + 1125$ or $53{\cdot}47 + 90$—is manufactured upon a very large scale, for the purposes of commerce, from common salt, which must first be converted into sulphate of soda in the manner described in page 427.

The dry sulphate of soda is to be mixed with its own weight of limestone or chalk, and half its weight of small coal, and the mixture being reduced to fine powder, is introduced into a reverberatory furnace, such as is figured in page 333, in charges of about 2 cwt. each. After being exposed to a full red heat for about an hour, on the floor of the furnace, the mass fuses, and being well stirred for a few minutes, is raked off through the opening in the side, and received in metal boxes. It forms a black mass, which is known in commerce as *black-ash*, or *British barilla*. The theory of this process is very remarkable; the sulphate of soda being melted in contact with the coally matter, is deoxidized, its oxygen being carried off by the carbon, and sulphuret of sodium remaining. This is immediately decomposed by the carbonate of lime, sulphuret of calcium and carbonate of soda being produced. $S.O_3 . Na.O.$ and $2C.$ form $2C.O_2$ and $Na.S.$, which, with $Ca.O..C.O_2$, gives $Ca.S.$ and $Na.O..C.O_2$. As, however, much of the carbonic acid of the chalk is expelled by the heat, a certain quantity of the soda remains caustic in the produce, and also some sulphuret of sodium undecomposed. This black-ash generally contains about 22 per cent. of real alkali. To obtain the soda under a purer form, the masses of black-ash are broken up, and digested in warm water until all soluble matter is extracted. The residue consists of sulphuret of calcium and the excess of coally matter. The liquor is then evaporated to dryness, and the saline mass obtained is calcined in a reverberatory furnace with one fourth of its weight of sawdust, in order to convert all of the alkali into carbonate, and to burn out some traces of sulphur which still remain; on being then redissolved in water, and the clear

solution dried down, it constitutes *white-ash*, or *soda-ash* of the best quality, containing from 45 to 50 per cent. of real alkali.

For the preparation of the crystallized carbonate, the soda-ash is dissolved in boiling water, and the solution being evaporated to a pellicle, is left to crystallize for some days. The mother liquor, when drained off the crystals, yields, when dried down, an inferior soda-ash, which is, however, applied to many manufacturing uses. The pure carbonate of soda crystallizes in flat, oblique rhomboidal prisms, as in the figure, which contain ten atoms of water, $Na..C.O_2+10\,Aq.$ In a dry atmosphere, they lose by efflorescence all their water, and fall into a white powder. It dissolves in five parts of cold, and in less than one of boiling water. By a gentle heat, the salt undergoes aqueous fusion, and when dried, gives a white powder, *soda siccata*. By a strong heat, the carbonate of soda melts, but is not otherwise affected.



Prior to the invention of the soda process described above, the carbonate of soda was obtained from the ashes of marine plants, as the salsola, and various fuci, which were burned in large quantities on the west coast of Ireland, in the Orkneys, and on the coasts of France and Spain. The saline products thus obtained were known in commerce as *kelp*, *barilla*, *varec ;* but these sources of alkali may now be considered as extinct. Graham states, on the authority of Mr. Muspratt, that in 1838 there were manufactured from common salt 50,000 tons of soda-ash and 20,000 tons of crystallized carbonate, and the manufacture is continually on the increase.

To the practical chemist and the manufacturer, it is important to be able to determine, by a rapid and easily executed process, the real quantity of alkali present in any sample of pearlashes or soda-ash that may be in the market. All such processes depend on measuring the quantity of sulphuric acid necessary to produce a neutral salt with a certain weight of the sample; but in the management of the details considerable difference may exist. A mode which I have found to be very accurate, and easily executed even by ordinary persons, consists in preparing beforehand a stock of a dilute sulphuric acid, of sp. gr. 1·068 at a temperature of 60°. This acid may be formed by mixing one ounce of the strongest oil of vitriol with nine ounces of water; but its sp. gr. should be verified by trial before being used.

One hundred grains of the sample to be tried are then to be powdered and stirred up in a capsule with an ounce of water. A glass jar about a foot high and an inch wide, provided with a lip to pour from and a steady foot, and graduated into 400 parts, of which each part indicates five grains of the standard acid, is to be filled with the acid up to the 400th mark, and then, by pouring very cautiously from the lip a few drops at a time, the alkaline liquor in the capsule is to be exactly neutralized. A little bit of litmus paper may be left in it, and stirred about well after each addition of a few drops of acid. A drop of acid in excess reddens the litmus paper permanently; and as this does not injure the result sensibly, it may be done in order to secure complete neutralization. The graduations of the glass being numbered from above downward, simple inspection shows how much acid has been employed; and it is only necessary to multiply the number of divisions by thirty-one if the alkali be soda, or forty-seven if the alkali be potash, and divide in each case by 100, to obtain the quantity of real alkali present in the 100 grains examined.

The principle of this method is, that 100 grains of the standard acid contain eight grains of dry sulphuric acid, and hence 100 measures contain forty grains, which number being that of the equivalent of the acid, neutralizes almost exactly thirty-one grains of soda or forty-seven grains of potash, which are the equivalent weights also. To find, therefore, the quantity of either alkali in a sample neutralized by, for example, 137 measures of acid, we say,

For potash, $100 : 47 :: 137 : x = \frac{137}{100} \times 47 = 64{\cdot}4$;

And for soda, $100 : 31 :: 137 : x = \frac{137}{100} \times 31 = 42{\cdot}5$.

A table may easily be constructed beforehand on those principles, so as to save even this little calculation. The greatest amount of error at all likely to occur in this process is one division of acid in excess. The difference made by this, however, does not influence the result for commercial purposes; thus, in the examples above taken, if the quantity of acid had been measured wrongly at 138, the indications would be, for potash, 64·9, and for soda, 42·8; the error in no case exceeding half a part per cent., and being exactly counterbalanced by taking the numbers 31 and 47 instead of the correct equivalents, 31·3 and 47·3.

Bicarbonate of Soda, $H.O..C.O_2+Na.O..C.O_2$, is formed by passing a current of carbonic acid gas through a cold solution of carbonate; the new salt precipitates in small opaque crystals, having the appearance of starch. It requires fifteen parts of cold water for its solution; it has an alkaline reaction, but is not disagreeable to the taste.

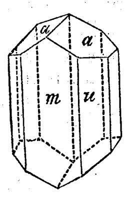
Sesquicarbonate of Soda occurs native on the banks of certain lakes in northern Africa, whence it is exported under the name of *trona*. Its formula is $2Na.O..C.O_2+3C.O_2+4H.O$. It cannot be formed at will.

Carbonate of Barytes.—$Ba.O..C.O_2$. This salt exists native, crystallized in oblique rhombic prisms; it is insoluble in pure water, but dissolves in water containing carbonic acid. It is very poisonous. It may be prepared artificially by mixing solutions of chloride of barium and carbonate of ammonia; a white precipitate falls, which, being well washed and dried, is pure carbonate of barytes. It is used in the analysis of minerals containing alkali, and for the preparation of various salts of barytes. It has been used in the manu facture of glass.

Carbonate of Strontia resembles perfectly the former.

Carbonate of Lime.—$Ca.O..C.O_2$. Eq. 632·5 or 50·7. The circumstances and forms under which this salt exists in nature have been so frequently noticed (p. 477, 225), and the molecular constitution and peculiar relations to light of its crystals so fully described, that it is not necessary to enter upon its history here farther. It may be prepared pure by decomposing chloride of calcium by means of carbonate of ammonia; it forms then a white powder insoluble in pure water, but dissolving in water containing carbonic acid. This is not due to the formation of a bicarbonate of lime, but owing to a specific solvent power which a solution of carbonic acid in water has on many bodies, as silica, phosphate of lime, &c., which are insoluble in pure water. It is thus that carbonate of lime is held dissolved in most waters, and is deposited as a crust on the interior of any vessels in which such water may be boiled. By the gradual dissipation of the carbonic acid on exposure to the air, the carbonate of lime may be slowly deposited, and then crystallizes; thus are formed the remarkable stalactites, &c., of limestone caverns.

Carbonate of Magnesia.—$Mg.O..C.O_2$. This salt exists anhydrous in nature, crystallized in rhombohedrons like calc spar. By dissolving magnesia in water by a stream of carbonic acid, it may be formed, and is gradually deposited in rhomboidal prisms of six or eight sides, as *m*, *u*, *a*, in the figure, which contain three atoms of water. It is this salt, $Mg.O..C.O_2+3$ Aq., which exists in Murray's solution of magnesia. When acted on by pure hot water, this salt is decomposed, carbonic acid escaping,



and basic carbonate of magnesia being produced. It is this basic carbonate which constitutes the *magnesia alba*, or common carbonate of magnesia of the shops. It is prepared by mixing boiling solutions of sulphate of magnesia and carbonate of soda, leaving the former slightly in excess. The precipitate is very light and bulky, and almost totally insoluble in water. One fourth of the carbonic acid is given off in this reaction, and the precipitate is found to be a compound of carbonate and of hydrate of magnesia, $Mg.O. . H.O. + 3 (Mg.O. . C.O_2 . H.O.)$, or $4Mg.O. + 3C.O_2 + 4$ Aq.

The nature of dolomite or magnesian limestone has been already sufficiently noticed (p. 348).

Carbonate of Manganese, $Mn.O. . C.O_2$, is a white powder formed by double decomposition, and decomposed by a red heat.

Protocarbonate of Iron, $Fe.O. . C.O_2$, exists native in rhombs iso morphous with calc spar. It may be prepared by decomposing protosulphate of iron by carbonate of soda; it forms a white precipitate, which, by exposure to the air, rapidly absorbs oxygen and gives out carbonic acid, becoming green, and ultimately red, being then mere peroxide of iron. The carbonate of iron can therefore scarcely be obtained pure; but by mixing the fresh precipitate with sugar, and evaporating to dryness with constant agitation, a quantity of the carbonate remains undecomposed, being protected from the air by a varnish of sugar on its particles, and thus constitutes the *carbonas ferri cum saccharo* of pharmacy. The carbonate of iron is soluble in water containing carbonic acid, and exists thus dissolved in chalybeate spas.

When solutions of sulphate of zinc and carbonate of soda are mixed together, a *basic carbonate of Zinc* is formed, consisting of $2 (Zn.O. . C.O_2) + 3Zn.O. . H.O.$ if the solutions were warm, but of $Zn.O. . C.O_2 + 2Zn.O. . H.O.$ if cold; carbonic acid gas is given off in both cases.

There are two *carbonates of Copper*, both basic; the green carbonate exists native (*malachite*), and is used as a pigment. It may be formed by mixing solutions of a salt of copper and an alkaline carbonate; the precipitate is at first flocculent, and of a fine pale blue, but when boiled it becomes dense, granular, and bright green: its formula is $2Cu.O. + C.O_2 + H.O.$ The blue carbonate exists also native (*Copper-azure*), but cannot be prepared artificially so as to be permanent: its formula is $3Cu.O. + 2C.O_2 + H.O.$

Carbonate of Lead, $Pb.O. . C.O_2$, exists native, crystallized in forms isomorphous with those of the carbonate of barytes, and may be formed as a finely-crystalline powder by decomposing solution of nitrate of lead by carbonate of soda. There are several basic carbonates of lead, which, in a greater or less degree of mixture, constitute the *White Lead*, or *Ceruse* of commerce, so much used in painting. The composition of white lead generally falls between those given by the formulæ $3Pb.O. + 2C.O_2 + H.O.$ and $4Pb.O + 3C.O_2 + H.O.$

For the manufacture of white lead, very thin sheets of the metal are exposed to the fumes arising from vessels containing weak vinegar, which are kept moderately warm by being imbedded in fermenting tan; the lead, absorbing oxygen from the air, combines

with the acetic acid, forming a basic acetate of lead, which is decomposed by the carbonic acid of the surrounding air, basic carbonate of lead being produced, and neutral acetate of lead remaining; this, under the action of the air, takes up a new quantity of lead, and the same decomposition is renewed, a minute quantity of acetic acid thus serving to produce a very large quantity of ceruse. This process has lately been much improved by exposing litharge, finely ground and mixed with one per cent. of acetate of lead, to a stream of carbonic acid, generally derived from the fermenting vats of a brewery; the one portion of neutral acetate successively unites with all the litharge to form basic acetate, the successive portions of which are decomposed by the carbonic acid, white lead being formed, and the original quantity of neutral acetate remaining uncombined at the end.

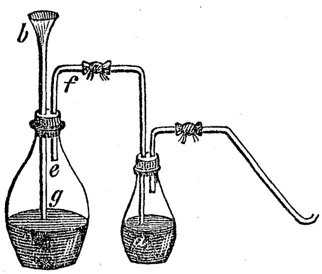
The carbonates of the other metals are unimportant.

Carbon combines with the metals to form *carburets*, of which the best known are those of iron and silver; the former has been fully noticed in the description of cast-iron and steel (p. 360), and the carburet of silver is a gray powder, which remains when certain silver salts of organic acids, as the citrate and tartrate, are imperfectly burned away.

Carbonic Oxide.—C.O. *Atomic Weight* 14·05?

If carbonic acid gas be passed through a tube containing red-hot charcoal, it takes up as much more carbon as it already contained, and forms carbonic oxide; its volume being thereby doubled. The gas may also be prepared by heating to redness, in an iron retort, a mixture of charcoal and chalk, when the carbonic acid evolved from the latter combines with the excess of carbon, and forms carbonic oxide; in place of charcoal, iron filings or zinc may be used; the metal, in this case, takes half of the oxygen from the carbonic acid, $C.O_2$ and Zn. giving Zn.O. and C.O.

A very simple and elegant way of obtaining this gas consists in warming strong oil of vitriol with crystals of oxalic acid, in a flask, *a b*, from which a tube, *f*, passes to a bottle containing solution of caustic potash, *a*, as in the figure; from this another tube conducts to the pneumatic trough. The oxalic acid, $C_2O_3 + H.O.$, yields up its basic water to the sulphuric acid, and, as the oxalic acid cannot exist except in combination with some base, it is resolved in carbonic oxide and carbonic acid ($C_2O_3 = C.O. + C.O_2$), which are evolved as gases, mixed in equal volumes; in bubbling through the bottle containing potash, the carbonic acid is completely absorbed, and the pure carbonic oxide may be collected over water.



It is a colourless, inodorous gas, and has no action on vegetable colours; it extinguishes a taper, but is combustible, and, burning with a pale blue flame, forms carbonic acid. It is this gas which produces, on the top of a clear coke fire, a blue flame, which ap-

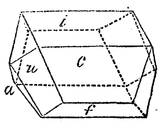
pears purple when seen with the red background of the glowing cinders. It contains half its volume of oxygen; its specific gravity is 972·8. Carbonic oxide appears to enter into union with a great variety of bodies, and to act in such compounds as a compound radical.

Oxalic Acid.—C_2O_3 or $2(C.O.)+O$. Eq. 451·2 or 36·1.

Oxalic acid is one of the most important organic bodies. It is found combined with potash, forming the *Salt of Sorrel*, in several plants of the genera oxalis and rumex, and combined with lime in the roots of rhubarb, and in a variety of lichens. It was formerly extracted principally from the oxalis acetosella, from whence its name is derived, but is now manufactured in larger quantities artificially. It is generally a product of the oxidation of vegetable substances by nitric acid, on which fact its mode of preparation is founded. The substances employed are usually starch or sugar, a quantity of which is placed in an earthen pipkin, of which a great number are arranged in a shallow vessel containing warm water; about four parts of nitric acid, specific gravity 1·42, are poured into each pipkin. The starch is rapidly oxidized, and nitrous fumes given off abundantly; when the action has become slow, one part more of acid is to be added, and the heat increased. The liquors so obtained, are mixed, evaporated to a pellicle, and set aside to crystallize, and the crystals are purified by re-solution and crystallization. From the mother liquors new quantities of oxalic acid may be obtained by heating with more nitric acid.

If we consider the sugar in its dryest form as being $C_{12}H_9O_9$, the action of the nitric acid should consist in first removing the nine equivalents of hydrogen, and substituting for them nine equivalents of oxygen; thus $C_{12}H_9O_9$ and $6N.O_5$ should give $6(C_2O_3)$ with 9H.O. and $6N.O_2$. But the action is not so simple, as other products, especially the *Saccharic Acid*, are at the same time formed. By means of permanganate of potash, however, the carbon of sugar may be very elegantly and directly changed into oxalic acid, $C_{12}H_9O_9$ and $6(Mn_2O_7+K.O.)$ producing $12(Mn.O_2)$ with 9H.O. and $6(C_2O_3+K.O.)$, the oxalic acid formed exactly neutralizing the potash of the manganic salt employed.

The oxalic acid crystallizes from its solution in oblique rhombic prisms, of which those planes marked *i c* are primary, and *a f* secondary: the summit is often dihedral, in which case the plane *a*, and that vertically opposite to it, are absent. These crystals contain three atoms of water, of which one is basic: $C_2O_3+H.O.+2\ Aq.$ When warmed, they give off 2 Aq., and the hydrate of oxalic acid remains as a white powder, which melts at 350°, and when heated farther sublimes, a portion being, however, decomposed; the products of the reaction of oil of vitriol on oxalic acid have been already noticed (p. 492). Oxalic acid is converted into carbonic acid by contact with many peroxides, as the peroxide of manganese, by which means the technical value of manganese ores may be determined (see p. 355). By contact with a great excess of hot nitric acid or of chlorine, it is also converted into carbonic acid.



The acidity of oxalic acid is very great; a grain of it dissolved in 30,000 grains of water will still affect litmus paper. It neutralizes the alkalies perfectly, and forms with them two series of acid salts. In the neutral oxalates, the oxygen of the acid to that of the base is 3 : 1. By heat, those of the metals proper are generally converted into carbonic acid and metal, $C_2O_3+M.O.$ giving C_2O_4 and M. Those of the earths and alkalies evolve carbonic oxide, and produce a carbonate, $C_2O_3+M.O.$ giving $C.O.$ and $C.O_2+M.O.$ The former action is usefully applied to obtain cobalt and nickel in the metallic state.

Oxalic acid is detected easily by its strong acidity, and its not leaving a carbonaceous residue when heated. Its solution gives, with lime-water, a precipitate which is insoluble in an excess of oxalic acid, or of any organic acid. It precipitates, also, the solutions of barytes and lead. It acts violently on animals as a poison; for an antidote magnesia is the best, but chalk or whiting is the most readily procured.

Several of the oxalates deserve special notice. There are three *oxalates of Potash*, remarkable as being the bodies by which Wollaston satisfied himself of the truth of the law of multiple combination, p. 208, their proportions of acid being as 1 : 2 : 4.

The *neutral Oxalate of Potash*, $K.O..C_2O_3+Aq.$, may be formed by acting on sugar by permanganate of potash, or by heating any fixed organic matter, as sawdust or paper, with an excess of potash, below redness. It is more simply produced by neutralizing oxalic acid, or the following salt, with carbonate of potash; it crystallizes in rhombic prisms, of a bitter taste, which dissolve in three parts of water, and are insoluble in alcohol.

Binoxalate of Potash, $K.O..C_2O_3+H.O..C_2O_3+2\ Aq.$, exists naturally in the various kinds of sorrel, from whence it was originally extracted under the name of *Salt of Sorrel*, but is now artificially made. One part of oxalic acid is exactly neutralized by potash, and then exactly as much more oxalic acid is added to the solution, from which, by evaporation and cooling, the salt crystallizes in oblique rhombic prisms, which are soluble in forty parts of cold and in six parts of boiling water. Its taste is strongly acid and saline, and it is poisonous, though less so than the acid uncombined. When heated, the salt is decomposed, evolving carbonic acid and carbonic oxide, and leaving a residue of carbonate of potash, which should be scarcely coloured if the salt were pure.

Quadroxalate of Potash, $K.O..C_2O_3+3H.O..C_2O_3+4\ Aq.$, is formed by neutralizing one part of oxalic acid by potash, and adding to the solution three times as much oxalic acid more. It may also be prepared by dissolving the binoxalate in muriatic acid, which takes half of the alkali, and the quadroxalate crystallizes out. This and the last salt are indiscriminately sold in commerce as salt of sorrel, and also often as *Salt of Lemons*, for removing iron moulds and stains of ink, which they do by forming, with the peroxide of iron, a soluble double salt.

There is but one *oxalate of Soda;* it is not important.

Oxalate of Lime, $Ca.O..C_2O_3+2\ Aq.$, exists abundantly in nature, forming the hard earthy basis of many lichens, and may be prepared

by mixing solutions of oxalate of ammonia and of any soluble salt of lime. It forms a white flocculent precipitate, which, by boiling, becomes heavy and granular. It is totally insoluble in water, and is hence used as a means of removing lime from solutions, and determining its quantity. It dissolves in the mineral acids, but is insoluble in all organic acids, even the acetic. When heated, it leaves a perfectly white residue of carbonate of lime.

The remaining simple oxalates are not important, except the *oxalate of Silver*, which is a white powder, prepared by double decomposition, and remarkable for being decomposed by a moderate heat, with a slight explosion, into carbonic acid and metallic silver.

There are several double oxalates of interest.

Oxalate of Potash and Peroxide of Iron, $(Fe_2O_3+3C_2O_3)+3K.O. \,.\, C_2O_3+6$ Aq., is prepared by dissolving peroxide of iron in solution of binoxalate of potash; it crystallizes in fine grass-green tables, which are permanent in the air. There exists a similar salt containing soda.

Oxalate of Potash and Chrome, $(Cr_2O_3+3C_2O_3)+3K.O. \,.\, C_2O_3+6$ Aq., is prepared by dissolving together in hot water one part of bichromate of potash, two of crystallized oxalic acid, and two of binoxalate of potash. A copious evolution of carbonic acid occurs, the chromic acid being deprived of half its oxygen by a part of the oxalic acid, with the remainder of which the oxide of chrome unites. The liquor assumes a fine purple colour, and on cooling, yields prisms of a splendid blue colour, so deep as to be perfectly opaque, unless the crystals be very thin.

Oxalate of Copper and Potash, $K.O. \,.\, C_2O_3+Cu.O. \,.\, C_2O_3+2$ Aq., is formed by digesting a solution of binoxalate of potash on oxide of copper. It crystallizes in fine blue prisms. It may be obtained with 4 Aq.

Chloro-carbonic Acid. — C.O. + Cl. Eq. 619·1 or 49·5. When equal volumes of carbonic oxide and chlorine are exposed for some hours to the light, they gradually combine, forming a colourless gas, which was termed by J. Davy, its discoverer, *Phosgene Gas*. Its odour is very irritating; the volume being diminished to one half, its density is 3412. It is decomposed by water, carbonic and muriatic acids being formed. It is decomposed by most metals, which unite with the chlorine and liberate carbonic acid. Its action on ammonia and on alcohol will be hereafter noticed.

Combination of Carbonic Oxide and Potassium, and the Products of its Decomposition.

If potassium be heated in a current of carbonic oxide, the gas is rapidly absorbed, but no charcoal is separated, as occurs with carbonic acid gas. The metal is converted into a blackish-green porous mass. If the air be admitted to this while hot, it inflames; when brought into contact with water, it is immediately decomposed, a peculiar gas being given off, and a rhodizonate of potash formed. This oxycarburet of potassium is obtained in quantity in the process by which potassium is procured, and constitutes the great obstacle to obtaining that metal, as described in page 337. It is also formed, but very impure, by merely brightly igniting cream of tartar in a covered crucible for an hour. The composition of this body is not yet known, and hence the mode of its decomposition cannot be expressed in formulæ. The gas which it evolves by solution in water has been examined by Mr. Davy. It is colourless and inflammable, and burns more brightly than olefiant gas. Its characteristic property is to detonate with a brilliant flash, and deposite charcoal when mixed with chlorine, even in the dark. He assigns to it the formula C_2H.

Rhodizonic Acid.—This is formed when the oxycarburet of potassium is dissolved in cold water. It is, when dry, isomeric with carbonic oxide, C_7O_7, but it appears to be a tribasic hydracid, and its formula $C_7O_{10}+H_3$. Its salts are of a fine scarlet red colour, whence its name.

Croconic Acid, C_5O_4, is formed when a solution of rhodizonate of potash is boiled; an atom of potash becomes free, and croconate and oxalate of potash are produced; $C_7O_7+3K.O.$ giving K.O. and $C_2O_3+K.O.$, with $C_5O_4+K.O.$ The salts of croconic acid are bright yellow coloured, but do not require other notice.

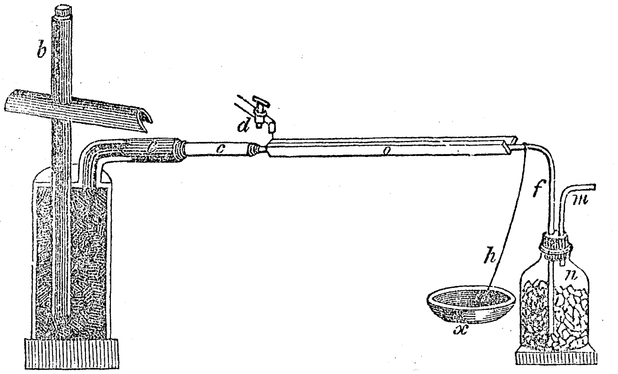
Mellitic Acid, C_4O_3, when dry, is found only native, combined with alumina, in a very rare mineral, *mellite* or *honeystone*. It crystallizes with water, $C_4O_3+H.O.$, and from its characters, especially the properties of the mellate of silver, it appears to be properly a hydrogen acid, having carbonic oxide as its radical, and its formula to be C_4O_4+H. When its ammonia salt is decomposed by heat, it is resolved into two very singular bodies, *paraban* and *euchroic acid*, whose history, however, is not important here.

In concluding this account of the oxygen compounds of carbon, it is proper to notice the peculiar function which the carbonic oxide appears to play. From the composition of its chlorine compound, it is certain that the equivalent of the gas is C.O., and, combining with oxygen, it forms carbonic acid, $C.O_2$. But I consider that we cannot look upon oxalic acid as being a lower degree of oxidation of the same radical as carbonic acid. On the contrary, the body C_2O_2, which is the basis of it, enters into a completely distinct series of compounds, such as oxamide, and is probably merely isomeric with carbonic oxide, into which it may be changed by a variety of reactions. Still less is carbonic oxide the basis of the rhodizonates, $C\,O_7$, or of the croconates or mellates; but the gas is changed into these more complex bodies by an isomeric action, which appears to occur at the moment that it combines with the potassium. I look upon the carbonic oxide gas, therefore, as being the basis only of carbonic acid and phosgene gas, and that the radicals of the oxalic acid and the bodies of its series, as well as of the rhodizonic and other acids, are compounds of carbon and oxygen, isomeric with carbonic oxide, but not yet isolated.

Of Sulphuret of Carbon.—$C.S_2$. Eq. 478·7 or 38·3.

This remarkable substance is formed whenever sulphur comes into contact with red-hot charcoal. It may be prepared by means of the apparatus figured in page 323; the tube *a*, *c* being filled with pieces of charcoal about the size of almonds, and bits of sulphur introduced from time to time at *h*, which is to be then tightly closed with a cork. The sulphur fuses, and the tube being a little inclined, runs down upon the ignited charcoal, combines with it, and the product passing as vapour into the long glass tube *e*, *f*, is condensed, and collected as a liquid in the bottle.

In large quantity, it is more conveniently prepared by fixing, air tight, into an iron cylinder about a foot high (such as a quicksilver bottle), two iron tubes, one long, *b*, reaching nearly to the bottom, and projecting a foot above the top, and the other short, *c*, and bent at a right angle, serving to convey the product to the condensing apparatus. By means of the tube *c*, the bottle may be filled with small fragments



of charcoal, and then, being placed in a furnace, the wide glass tube *c*, and the narrower *f*, are to be attached by corks. From the cock *d* a stream of water flows, which, guided by the tin-plate gutter *o*, cools the tube *f*, and is conducted by the thread *h* to the basin *x*. When the bottle is bright red, small pieces of sulphur are to be dropped in by the long tube, the end of which is to be then carefully closed up by a cork. The sulphur, being vaporized, acts on the charcoal, and the sulphuret of carbon formed being condensed in the narrow tube *c f*, collects in the bottle *n*, which is half filled with ice in order more perfectly to preserve it. Any incondensible gases that may be formed escape by the tube *m*. The process might be continued until all the charcoal in the bottle had been converted into sulphuret; but if sulphur were allowed to be present to excess, it would melt the bottom of the bottle. The process, therefore, should not be pushed so far.

The sulphuret of carbon thus obtained contains an excess of sulphur dissolved in it, and must be purified by redistillation at a very moderate heat (in a water bath); when about nine tenths have distilled over, by allowing the residue to evaporate spontaneously in a capsule, very fine right rhombic crystals of sulphur may be obtained (p. 284).

The sulphuret of carbon is a colourless liquid, of a very disagreeable garlic smell. It does not mix with water, but dissolves in alcohol and ether. It dissolves sulphur and phosphorus in large quantity. Its specific gravity is 1·272. It boils at 108° Fah., and forms a colourless vapour, whose specific gravity is 2·621. From its volatility, it obtained the name of *Alcohol of Sulphur*. In evaporating it produces great cold; mercury may be frozen by suspending under a bell-glass a thermometer, the bulb of which is enveloped by cotton moistened by this fluid, and rapidly exhausting the air. It is very inflammable, burning with a blue flame, and producing carbonic and sulphurous acids. If a few drops of it be let fall into a strong bottle containing oxygen, so much of it evaporates as to form an explosive mixture with the gas, which then detonates when touched with a lighted taper, like a mixture of oxygen and hydrogen. When the sulphuret of carbon is heated in contact with a metal, carbon is separated, and a metallic sulphuret produced. It is thus found to consist of one atom of carbon united to two of sulphur, and its formula to be $C.S_2$.

It is a powerful sulphur acid, combining with the sulphurets of the alkaline metals and forming sulphur salts, which are crystallizable; with the sulphurets of lead, silver, copper, &c., it forms in-

soluble compounds, which correspond closely in composition to the ordinary carbonates. This substance is, in fact, exactly equivalent to carbonic acid, $C.O_2$, the sulphur being replaced by oxygen, with which its analogies have been already noticed in p. 291. The sulphuret of carbon is hence often called *Sulphocarbonic Acid.*

Moist chlorine converts this body into a crystalline substance like camphor; but this, as well as the products of the action of nitric acid and of strong alkalies, have not yet been accurately examined

Chlorides of Carbon.

Subchloride of Carbon, $C_2Cl.$, is formed by passing the vapour of the protochloride many times through an ignited glass tube; chlorine is given off, and the subchloride deposited in silky crystals, which are fusible, and sublime at about 300° unchanged.

Protochloride of Carbon, C_2Cl_2, is also formed from the sesquichloride of carbon by heating its vapour to redness, when chlorine is given off; or better by distilling the sesquichloride with an alcoholic solution of sulphuret of potassium, which removes one third of the chlorine. It is a limpid fluid, boiling at 160°; the sp. gr. of its vapour is 2862. By a strong heat it gives subchloride and free chlorine.

Sesquichloride of Carbon, C_2Cl_3, is produced by the action of a great excess of chlorine in bright sunshine on olefiant gas or on muriatic ether; all the hydrogen of these bodies is removed, and the carbon remains united with chlorine. It forms a white crystalline mass like camphor, which is insoluble in water, but soluble in alcohol and ether. It melts at 320°, and sublimes at 360° unchanged; at a red heat it abandons chlorine, and forms the bodies last described.

Bichloride of Carbon, C_2Cl_4, is formed by exposing a body termed chloroform, whose formula is $C_2H.Cl_3$, or marsh gas, C_2H_4, to an excess of chlorine in bright sunlight. The hydrogen is gradually removed and replaced by chlorine. It is liquid; its sp. gr. is 1·6; it boils at 192°. The sp. gr. of its vapour is 5302.

CHAPTER XVIII.

OF THE COMPOUNDS OF NITROGEN AND HYDROGEN. AMMONIA, ITS DERIVATIVES AND COMPOUNDS.

ALTHOUGH there is very perfect evidence that hydrogen and nitrogen unite in two, perhaps in three proportions, we as yet know but one of these in an isolated form, which is the *volatile alkali*, *Ammonia.* This was known to the earliest chemists, but the importance of its history to the progress of chemical philosophy has been but lately felt to its just extent.

Ammonia is produced in almost all reactions where nitrogen and hydrogen are brought together, one or both being nascent. Thus, when an electric spark is passed through damp air, nitric acid and ammonia are both formed, and hence the rain which falls after thunder-storms contains nitrate of ammonia. It is evolved in large quantities in the putrefaction of organic substances containing nitrogen, and is formed also by their distillation at high temperatures, whence the greater supply of ammonia used in the arts is derived When any oxide of nitrogen is mixed with hydrogen, and passed through a tube containing red-hot spongy platinum, ammonia is formed; and, lastly, it is produced abundantly when iron or tin is

oxidized violently by nitric acid, the oxygen being taken both from the acid and water, the nascent hydrogen and nitrogen unite. Ammonia is also a product of organization, being contained in the sweat of animals, and being exhaled by the flowers of many plants, and by the leaves, also, of the cruciferæ.

For the purposes of the chemist, ammonia is obtained from the muriate of ammonia, or sal ammoniac, which is manufactured in large quantities for commerce, by processes to be hereafter described. Equal parts of the sal ammoniac, in powder, and slacked lime are to be intimately mixed and heated in a flask, from which a bent tube passes; the gas which issues is to be conducted through a tube, as in the figure (p. 310), containing dry lime or fused potash, by which adhering moisture is removed, and it may then be collected over mercury. It is colourless and transparent. Its odour is strong, pungent, and irritating, well known as the smell of hartshorn. When perfectly dry, it has no action on vegetable colours; but if damp, it reacts powerfully alkaline. The brown colour which it produces on turmeric disappears when heat is applied, by which it is distinguished from the browning by the fixed alkalies or earths. By a pressure of $6\frac{1}{2}$ atmospheres, or at a temperature of $-61°$, gaseous ammonia is liquefied. When inspired pure, it proves excessively caustic and poisonous.

Ammonia is slightly combustible. It does not support combustion. When a series of electric sparks is passed through a quantity of the gas confined over mercury, its volume enlarges, and ultimately becomes double. It is then totally decomposed, and the resulting gas consists of three volumes of hydrogen and one of nitrogen: the specific gravity of ammonia is therefore 591·5, as deduced in p. 215, and its formula $N.H_3$. If a current of ammoniacal gas be passed through a red-hot tube filled with iron wire, it is decomposed in the same way as by electricity. If the tube contain red-hot charcoal, carbon is taken up, and prussiate of ammonia and carburet of hydrogen produced.

Ammoniacal gas is rapidly absorbed by water, which takes up 780 times its volume at 32°. Great heat is thereby evolved, and the solution, which augments two thirds in volume, has a specific gravity of 0·872, and boils at 120°. It contains then about 32 per cent. of ammonia, and approximates to the formula $N.H_3+4$ Aq. This solution is termed *Water of Ammonia*, or, improperly, *Liquid Ammonia*. To prepare it upon a larger scale, the matrass and series of three-necked bottles, described and figured in p. 308, may be employed. Five parts of lime, slacked, and mixed with as much water as will convert it into a thin paste, are to be introduced, with four parts of powdered sal ammoniac, into the matrass, which is then to be placed upon the sand-bath, and connected with the range of bottles. The first bottle is left empty, in order to catch any water or mixture that may be carried over, and it should be allowed to grow warm, in order that it may retain no gas; in the other bottles water is placed, by which the gas is absorbed, and they are kept cool by damp cloths applied to their surface. For ordinary purposes, water of ammonia need not contain more than 18 per cent. of gas; it then has a specific gravity of 0·930.

The watery solution of ammonia possesses all the characters of the gas in a strong degree. It neutralizes the strongest acids, and acts in all respects as a strong base, ranking next to lime. It forms many classes of combinations, in some of which it exists unaltered, but in others it first undergoes peculiar decomposition. Its action on chlorine is very violent, and accompanied by flame; sal ammoniac is formed and nitrogen set free, as described in p. 261.

Ammonia is very easily recognised: its odour, the brown colour given to turmeric paper, which is removed by a gentle heat, and its forming dense white fumes on the approach of a glass rod moistened with strong muriatic acid, characterize it when free; all substances which contain ammonia are either volatilized by heat, or decomposed, the ammonia being generally liberated; in all cases, by heating the body with moist caustic potash, ammonia is evolved as gas, and may be known by the properties now described.

The real nature of ammonia has recently been the subject of much inquiry; its equivalent is satisfactorily determined to be 17·1, and hence its formula is $N.H_3$, and its equivalent volume 4. It may enter into combination directly with dry oxygen acids, but it does not then form the proper ammoniacal salts, which all contain an atom of water essential to their constitution. It combines with a great number of saline bodies, and then resembles, in its functions, their water of crystallization. Its most remarkable property, however, is, that, in acting on metallic compounds, and on certain organic acids, it abandons an atom of hydrogen, and the remaining $N.H_2$ combines with the metal, or with the radical of the acid. Thus, with Hg.Cl. and $N.H_3$ there result $Hg.N.H_2$ and H.Cl.; with $Pt.Cl_2$ and $2N.H_3$ there are formed $Pt. + 2N.H_2$ and 2H.Cl.; from $Hg..N.O_6$ and $N.H_3$ are produced $Hg.N.H_2$ and $H.N.O_6$. Of organic bodies, oxalate of ammonia gives, when heated, $C_2O_2 + N.H_2$, and benzoate of ammonia produces similarly $C_{14}H_5O_2 + N.H_2$. It is hence evident that the third atom of hydrogen is not so intimately combined with the nitrogen as the remaining two; it may be eliminated by the simplest reactions, but the N. and H_2 remain much more firmly united, and separate only when the constitution of the ammonia is totally broken up. I hence concluded that the $N.H_2$ should be considered as the radical of ammonia, and proposed to term it *Amidogene*, and its symbol Ad. The ammonia is then *Amidide of Hydrogen*, and its rational formula $N.H_2H.$ or Ad.H. Ammonia is thus assimilated to water, and to chloride of hydrogen in constitution, the radical amidogene having the closest analogy to oxygen and chlorine. These conclusions have been almost unanimously adopted by chemists.

These views are remarkably illustrated by the action of ammonia on potassium; when this metal is heated in the dry gas, hydrogen is disengaged, and a fusible olive-green substance is obtained. The quantity of hydrogen evolved is the same as that which the metal should evolve from water, that is, one atom, and the olive body consists of $K.N.H_2$. It is *Amidide of Potassium*. When put into water, potash and ammonia are produced, K.Ad. and H.O. giving K.O. and H.Ad. When this olive substance is heated nearly to redness, ammonia is expelled and *Nitruret of Potassium* remains, $3K..N.H_2$ giv-

ing $2N.H_3$ and K_3N. The phenomena are exactly the same with sodium, an amidide and a nitruret of sodium being thus formed.

In describing the compounds of ammonia, it is necessary to distinguish those in which ammonia acts simply as amidide of hydrogen, resembling in its functions the oxide or chloride of hydrogen, from the class of bodies in which the ammonia is associated with water, the proper salts of ammonia, which, as already noticed, are isomorphous with those of potash. I shall have occasion to discuss the theory of these bodies farther, but shall first describe the most important members of the former class.

Ammonia and Chlorine.—If a bottle full of chlorine gas be inverted in a cup containing a solution of sulphate or muriate of ammonia, it is gradually absorbed, and a heavy yellow liquid collects in globules in the bottom of the cup. This substance must be treated with the utmost caution; if strongly rubbed or struck, or if it be touched with any greasy body, or with phosphorus, it explodes with intense violence; a globule as large as a pin-head, on being exploded in a teacup, shatters it to pieces. Almost every chemist who has examined it has been severely hurt, and hence its composition is not yet well known. Sir Humphrey Davy found that, when decomposed over mercury, it gives nitrogen and chlorine in the proportions by volume of 1 : 3, and hence it was concluded to be *Chloride of Azote*, $N.Cl_3$, under which name it is described in most books. It has been observed, however, that traces of sal ammoniac are formed when it is decomposed; it consequently must contain hydrogen, and it may probably be *bichloride of Amidogene*, $Ad.Cl_2$, which, when decomposed, should produce N. and Cl_3, besides Ad.H. . H.Cl.

Iodine and Ammonia.—When the semi-fluid compound of iodine and ammonia is put into water, it is decomposed into hydriodate of ammonia, and a brown powder which is usually described as *Iodide of Azote*, $N.I_3$. This substance may also be prepared by digesting iodine in water of ammonia, the iodine gradually changing into the brown substance, and the solution containing hydriodate of ammonia: this body must be collected on filters in very small quantity, and dried merely by exposure to the air; if it be rubbed, even under water, it explodes with a violent detonation, though not so powerfully as the previous body. The cloud of hydriodate of ammonia, formed by its decomposition, is very evident; it therefore contains hydrogen, and I look upon it as a *biniodide of Amidogene*, $Ad.I_2$.

A corresponding compound containing bromine has been formed.

By the action of ammonia on metallic oxides, a numerous class of bodies may be formed, which all possess more or less violent detonating properties; they all contain combined water. It is impossible to say, positively, whether the ammonia exists undecomposed in these bodies; I rather think it does, and I shall hence term them *ammoniurets*.

Ammoniuret of Silver.—This is the most violent of all these compounds: it is prepared by digesting recently-prepared oxide of silver in water of ammonia, or by dissolving nitrate of silver in an excess of water of ammonia, and precipitating the solution by caustic potash. It is a brown powder, which detonates violently by the slightest shock or friction; when exploded, it is said to produce

water, azote, and metallic silver, which should give for its formula $N.H_3+3Ag.O.+Aq.$ But the facility of its decomposition, which has been the cause of many serious accidents, has prevented it being accurately analyzed.

Ammoniuret of Gold, $Au.O_3+2Ad.H.$, is produced by the action of water of ammonia on peroxide of gold. It is a brown powder, nearly as explosive as the former body, but it has been accurately analyzed by Dumas. These bodies are known as *Fulminating Gold* or *Silver*.

The *Ammoniuret of Platinum* is formed by digesting hydrated oxide of platinum in water of ammonia. It is a light-brown powder, not yet analyzed, and quite different from the impure substance described in books as Davy's fulminating platinum.

I have examined the *ammoniurets of Copper and Mercury* formed by digesting the oxides of these metals in water of ammonia: the first is blue, the second yellow; their formulæ are $3Cu.O.+2Ad.H.+6$ Aq., and $3Hg.O+Ad.H.+2$ Aq. They detonate feebly when heated. There exist, also, compounds of ammonia with the oxides of uranium, of iron, and of osmium, which have not been accurately examined.

By the action of heat on some metallic compounds of ammonia, true nitrurets of the metals have been obtained, of which the most remarkable are those of copper and mercury. The *nitruret of Copper* was formed by passing ammonia over anhydrous oxide of copper at a temperature of 480° Fah.; water is evolved, and the nitrogen and copper unite, forming a black powder, which, at the temperature of 540°, is decomposed, with the evolution of a red light, into its elements. Its formula appears to be $Cu_6N.$, which corresponds to the suboxide $Cu_2O.$, as when replacing oxygen $\frac{N}{3}$ is equivalent to O. (see p. 262) and $Cu_6N.=3(Cu_2+\frac{N}{3})$. Schrœter, to whom the discovery of the above compound is due, formed also a *nitruret of Chrome*, whose formula is not quite ascertained.

Ammonia is absorbed in large quantities by the chlorides of phosphorus and of sulphur, and substances produced which possess singular properties.

Ammoniacal Protochloride of Phosphorus, $P.Cl_3+5Ad.H.$, is obtained by exposing the liquid chloride of phosphorus to a current of dry ammonia. It forms a white powder, which, when put in contact with water, produces sal ammoniac, and an insoluble white substance that has not been analyzed; the reaction is probably that $3(Cl.H..Ad.H.)$ and $P.N_2H_3$ result. If the ammoniacal protochloride of phosphorus be calcined without access of air, a very remarkable body, *phosphuret of Azote*, the formula of which is $P.N_2$, is produced, while phosphorus, hydrogen, ammonia, and sal ammoniac are expelled. The phosphuret of azote is insoluble in water, and resists the action of the most powerful acids and alkalies. The composition of the *ammoniacal perchlorides of Phosphorus* is not quite certain, as these bodies appear to decompose each other. The formula is $P.Cl_5+2Ad.H.$ When calcined they yield phosphuret of azote.

Gaseous ammonia and chloride of sulphur combine in two proportions, according as each ingredient is in excess. The formulæ of these bodies are $S.Cl.+Ad.H.$ and $S.Cl.+2Ad.H.$ The former is a brown powder, soluble in alcohol and ether; the latter is a citron-yellow powder. They are remarkable for delivering as a product of their decomposition, by water or by heat, the *sulphuret of Azote* ($S_3N.$), which is a volatile yellow powder, decomposed by the prolonged action of water into ammonia and hyposulphurous acid, $2(S_3N.)$ and $6H.O.$ giving $3S_2O_2$ and $2Ad.H.$

When chloride of sulphur is digested with water of ammonia, a brown substance is formed, whose composition is $Cl.S_4.N_3H_6$. It is probably formed of chloride and amidide of sulphur, $S.Cl.+3(S.Ad.)$

Ammoniacal gas is absorbed in great quantity by the volatile chlorides of boron, arsenic, tin, and titanium. The compounds formed are white and crystalline; they are decomposed by water, and the solution contains sal ammoniac, and the metal or the boron, in combination with oxygen.

There are few metallic salts which do not absorb ammonia when exposed to a current of the dry gas; but certain metals are specially distinguished by the character that ammonia added to their solutions produces precipitates which either contain ammonia or amidogene, as is the case with mercury, palladium, and platinum, or by an excess of the ammonia the precipitate is redissolved, and soluble compounds containing ammonia are produced, as occurs with zinc, copper, nickel, cobalt, and also palladium and platinum. The number of combinations thus formed is so very

great that it would be tedious to describe all, and I shall hence notice only such as possess scientific or pharmaceutical importance.

1. *Ammonia-Salts of Zinc.*

Dry sulphate of zinc exposed to a current of dry ammonia absorbs it, producing a white powder, $2(\mathrm{Zn.O.\,.\,S.O_3})+5\mathrm{Ad.H.}$, which dissolves perfectly in water.

If water of ammonia be added to a solution of chloride of zinc, a basic chloride is precipitated, which being redissolved by an excess of ammonia, a colourless solution is obtained, which crystallizes on cooling. According to the proportion of ammonia in excess, I have found that one or other of two compounds may be formed, one in long and brilliant prisms, the other in fine pearly tables. The latter salt consists of $\mathrm{Zn.Cl.}+2\mathrm{Ad.H.}+\mathrm{H.O.}$, the former of $2(\mathrm{Zn.Cl.})+2\mathrm{Ad.H.}+\mathrm{H.O.}$ In these salts, as in all such as are produced by the action of an excess of ammonia on a metallic salt, I consider that the acid exists combined with ammonia, and not with the metallic oxide, in which they differ essentially from those produced by the direct absorption of ammonia by a salt, in which I conceive the union of the acid and oxide not to be disturbed. Hence I write the formula of the *tabular ammonia-chloride of Zinc* as $\mathrm{Ad.H.\,.\,H.Cl.}+\mathrm{Ad.H.\,.\,Zn.O.}$ When heated it gives off ammonia and water, and a white powder, $\mathrm{Ad.H.\,.\,Zn.Cl.}$, remains.

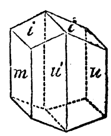
By the action of an excess of ammonia on a solution of sulphate of zinc, the *ammonia sulphate of Zinc* is formed: its formula is $\mathrm{Ad.H.\,.\,H.O.\,.\,S.O_3}+\mathrm{Ad.H.\,.\,Zn.O.}$ It crystallizes in short prisms; when heated it evolves $\mathrm{Ad.H.\,.\,H.O.}$, and a white powder, $\mathrm{Ad.H.\,.\,Zn.O.\,.\,S.O_3}$ remains. In crystals it contains 3 Aq., of which it loses two by efflorescence, and the third by a moderate heat.

2. *Ammonia-Salts of Copper.*

Chloride of copper absorbs dry ammonia, forming a blue compound, $\mathrm{Cu.Cl.}+3\mathrm{Ad.H.}$, soluble in water.

When ammonia is added to a strong and hot solution of chloride of copper, until the precipitate which first forms is perfectly redissolved, a deep purple liquor is produced, from which octohedral crystals are deposited on cooling. Their formula is $\mathrm{Ad.H.\,.\,H.Cl.}+\mathrm{Ad.H.\,.\,Cu.O.}$ When heated, these crystals evolve ammonia and water, and a blue powder, $\mathrm{Ad.H.\,.\,H.Cl.}$, remains, which is totally decomposed by a strong heat.

Dry sulphate of copper exposed to a current of dry ammonia forms a fine purple powder, whose formula is $2(\mathrm{Cu.O.\,.\,S.O_3})+5\mathrm{Ad.H.}$



An excess of ammonia gives, with a strong solution of sulphate of copper, a rich purple liquor, from which the *ammoniacal sulphate of Copper* crystallizes on cooling in large right rhombic prisms, *u*, *u'*, with dihedral summits, *i*, *i*, as in the figure, *m* being a secondary plane. I consider these crystals, however, to be macles. The formula of this salt is $\mathrm{Ad.H.\,.\,H.O.\,.\,S.O_3}+\mathrm{Ad.H.\,.\,Cu.O.}$ When heated, it gives off ammonia and water, and a green powder, $\mathrm{Ad.H.\,.\,Cu.O.\,.\,S.O_3}$, remains.

Under the name of *cuprum ammoniatum*, the ammoniacal sulphate of copper is employed in medicine. It is then prepared by rubbing together sulphate of copper and carbonate of ammonia in a mortar. The mass becomes pasty, owing to the water of crystallization of the sulphate of copper becoming free, and carbonic acid is given off. The purple mass which results is soluble in water, and generally contains carbonate of ammonia in excess.

When a hot and strong solution of nitrate of copper is decomposed by an excess of ammonia, and allowed to cool, the *ammoniacal nitrate of Copper* crystallizes in rhombic octohedrons of a fine purple colour: its formula is $\mathrm{Ad.H.\,.\,H.O.\,.N.O_5}+\mathrm{Cu.Ad.}$ In this body there is no doubt of the metal being combined with amidogene, and not the oxide with ammonia; hence probably arises its remarkable character of deflagrating violently when heated until it begins to melt.

The iodide and fluoride of copper produce compounds resembling those of the chloride.

3. *Ammonia-Salts of Nickel and of Cobalt.*

These resemble the corresponding salts of copper so perfectly, that it is sufficient to refer to the foregoing for their properties; and their composition is obtained by substituting Ni. or Co. for Cu. in the formulæ.

4. *Ammonia-Salts of Silver.*

The chloride of silver is soluble in water of ammonia. The solution gives opaque white rhombic crystals, which exhale ammonia when exposed to the air, and leave chloride of silver.

When the sulphate or the nitrate of silver is treated with an excess of water of ammonia, colourless solutions are obtained, which yield by evaporation double salts, in rhombic prisms, having the formulæ Ad.H..H.O..S.O_3+Ag.Ad. and Ad.H..H.O..N.O_5+Ag.Ad. In both salts the silver is combined with amidogene. Chromate of silver and ammonia gives a similar salt. The ammonia-nitrate of silver is employed in testing for arsenic and in preparing fulminating silver. A remarkable property of it is, that when fused it evolves ammonia and nitrogen, and metallic silver remains mixed with ordinary nitrate of ammonia, and coats the sides of the glass containing it with a brilliant mirror surface. By a higher temperature the nitrate of ammonia is decomposed, and nitrous oxide evolved.

5. *Ammonia-Salts of Palladium.*

This metal is remarkable for giving with ammonia two series of salts, of which one is soluble and the other insoluble in water.

When ammonia is added to a solution of protochloride of palladium, a flesh-coloured precipitate is produced, having the formula Pd.Cl..Ad.H. When more ammonia is added, it dissolves, and from the solution the second salt crystallizes in long rectangular prisms, having the formula Ad.H..H.Cl.+Pd.O..H.Ad. By a gentle heat, an atom of water is given off, and the metal exists then in the salt as amidide. If, in a solution of this salt, the excess of ammonia be neutralized by muriatic acid, a yellow crystalline precipitate forms, which has the same formula as the first salt, Pd.Cl.+H.Ad.

With solution of sulphate of palladium and water of ammonia, a precisely similar series of salts is formed; the first being flesh-red, Pd.O..S.O_3+H.Ad.; the second salt in colourless prisms, Ad.H..H.O..S.O_3+Pd.O..H.Ad., and, when dried, the last member becoming Pd.Ad.; and by a small quantity of an acid, a crystalline precipitate, which consists also of Pd.O..S.O_3+H.Ad.

The iodide of palladium gives similar salts. With the nitrate no other than the colourless crystalline salt can be obtained, whose form is thin rhombic plates, Ad.H..H.O..N.O_5+Pd.Ad. When heated, it deflagrates like loose gunpowder, and leaves behind metallic palladium as a black powder.

In the red and yellow insoluble ammonia-salts of palladium, although the experimental composition is the same, I consider that an important difference of constitution exists. The red salts are formed by adding ammonia to a simple salt of the metal; direct union then occurs, and we have, for example, Pd.Cl.+H.Ad. But when we form the yellow salt by adding an acid to a solution of the soluble ammonia-salt, I conceive that the acid unites directly with the amidide of the metal, and thus forms, for example, Pd.Ad.+H.Cl. The yellow ammonia-iodide, Pd.Ad.+H.I., gradually changes itself back into the red substance, Pd.I.+H.Ad.

6. *Ammonia-Salts of Mercury.*

From the great influence these bodies have had on the theory of ammonia, and their importance in pharmacy, the mercurial compounds containing ammonia deserve more detailed notice than those of any other metal.

A. *Action of Ammonia on the Haloid Salts of Mercury.*

When corrosive sublimate is heated in a current of dry ammoniacal gas, it unites therewith, forming a white compound, fusible and volatile, having the composition 2Hg.Cl.+H.Ad. By contact with water, this body is decomposed into sal alembroth and white precipitate; the former, a compound of sublimate and sal ammoniac, dissolving, and the latter, whose composition will be next studied, separating as a white powder.

If we add to a cold solution of corrosive sublimate a very slight excess of ammonia, a copious white precipitate is produced, and the liquor is found to contain exactly half the chlorine of the sublimate combined with hydrogen and ammonia as sal ammoniac; the white powder, which had been known to the early chemists as *White Precipitate of Mercury*, contains all the mercury and the remaining half of the chlorine of the sublimate. It was supposed to contain, also, ammonia and oxygen, but I have proved that it contains only the elements of amidogene and no oxygen; that its

formula is Hg.Cl.+Hg.Ad., it being a true chloro-amidide of mercury. The theory of its formation is very simple, 2Hg.Cl. and 2H.Ad. producing, by interchange of the elements of one equivalent of each body, Hg.Cl.+Hg.Ad., which precipitates, and H.Cl.+H.Ad., which remains dissolved. This was the first instance in which amidogene was discovered to be combined with a metal, and from its establishment, the true constitution of ammonia was first recognised.

White Precipitate is insoluble in cold water. It is decomposed by boiling water, two atoms of which, reacting on two of white precipitate, produce sal ammoniac, which dissolves, and a heavy yellow powder, which is insoluble in water, and has the formula Hg.Cl.+2Hg.O.+Hg.Ad. This body is completely analogous to the oxychloride of mercury, Hg.Cl.+3Hg.O., from which it may be prepared by the action of ammoniacal gas, the third atom of Hg.O. and H.Ad. giving Hg.Ad. and H.O., which is expelled. When white precipitate is heated suddenly, it is totally converted into calomel, nitrogen, and ammonia, but by careful management of the heat, sublimate and ammonia are given off, and a red powder remains, which is a compound of chloride and nitruret of mercury, Hg.Cl.+Hg_3N.; or, rather, as the nitrogen here replaces oxygen, and has hence the one third atomic weight, Hg.Cl.+3Hg.$\frac{N}{3}$, exactly analogous to the oxychloride; by careful management, all the sublimate may be expelled, and the *azotured of Mercury*, Hg.$\frac{N}{3}$, is obtained as a brown powder, which detonates with great violence when struck.

The white precipitate which has been now described must be distinguished from another body which has been confounded with it in the pharmacopœias, until the difference was shown by Woehler's observations and my analysis. This second or beta-white precipitate is prepared by adding caustic potash to a cold solution of the double salt formed by corrosive sublimate and sal ammoniac. It may also be formed by boiling alpha-white precipitate in a solution of sal ammoniac. It has a crystalline aspect, and is not decomposed by boiling water; when heated, it fuses, and gives off ammonia and azote, while a mixture of calomel, sublimate, and sal ammoniac sublimes. Its formula is very simple, Hg.Cl.+H.Ad.; but it may also be looked upon as a compound of alpha-white precipitate and sal ammoniac, (Hg.Cl.+Hg.Ad.)+(H.Cl.+H.Ad.)=2(Hg.Cl.+H.Ad.).

When calomel absorbs dry ammonia, it forms a dark gray powder, which is 2 Hg_2Cl.+H.Ad.; by a gentle heat all ammonia may be expelled, and the calomel remains quite white.

If the calomel be, however, digested in water of ammonia, one half of its chlorine is converted into sal ammoniac, and a dark gray powder results, which is a compound of subchloride and subamidide of mercury, Hg_2Cl.+Hg_2Ad. This body, which I have termed *Black Precipitate*, is formed by a similar reaction to that by which alpha-white precipitate is produced, 2Hg_2Cl. and 2H.Ad. giving Hg_2Cl.+Hg_2Ad. and H.Cl.+H.Ad. By several chemists, the action of water of ammonia on calomel is given as a means of preparing black oxide of mercury, which is quite incorrect. The compound formed contains no oxygen.

The action of the bromides of mercury with ammonia has not been so minutely studied as that of the chlorides; it is known, however, that bromide of mercury gives with water of ammonia a white precipitate, consisting of bromide and amadide, Hg. Br.+Hg.Ad., and analogous to the alpha-white precipitate. The subbromide of mercury produces with water of ammonia a black powder, consisting of Hg_2Br.+Hg_2Ad.

Iodide of mercury dissolves plentifully in hot water of ammonia, and the solution deposites, on cooling, long prisms of a snow-white colour, which, however, rapidly exhale ammonia when exposed to the air, and leave red iodide of mercury in pseudomorphous crystals. This white body has the formula 2Hg.I.+H.Ad.

There is no iodine compound analogous to alpha-white precipitate; but when that substance is warmed in a solution of iodide of potassium, ammonia is evolved and a brown powder is formed, having the formula Hg.I.+2Hg.O.+Hg.Ad.

B. *Action of Ammonia on the Oxygen Salts of Mercury.*

When sulphate of mercury is digested in water of ammonia, it is converted into a white substance, to which I have given the name of *ammonia-turpeth*. It is not acted on by water nor by alkalies. Its formula is 3Hg.O.+S.O_3+Hg.Ad. It is therefore ordinary turpeth mineral combined with amadide of mercury.

When water of ammonia is added to a solution of nitrate of mercury, being cold and not in excess, a white precipitate is formed, *a basic ammonia-nitrate*, which is found to consist of H.Ad. . N.O_5+3Hg.O. It is therefore a basic nitrate of mercury, analogous to the ordinary basic nitrate, H.O. . N.O_5+3Hg.O., except that am-

monia (amidide of hydrogen) is substituted for water (oxide of hydrogen). If an excess of ammonia be added, and the mixture boiled, the white precipitate becomes heavier and granular, and is then found to consist of Hg.Ad. . $N.O_5$+3Hg.O. This substance, the *β basic ammonia-nitrate*, is evidently analogous to the former, the hydrogen being replaced by mercury, and it corresponds accurately in constitution also to the ammonia-turpeth.

If either of these basic ammonia-nitrates be boiled in water containing much nitrate of ammonia, they dissolve and form double salts; that usually formed is in short opaque white prisms, having the very simple composition 4Hg.O.+3(H.Ad. . H.O. . $N.O_5$); but as it is decomposed by water into the β basic ammonia-nitrate, its formula must be (Hg.Ad. . $N.O_5$+3Hg.O.)+2(H.Ad. . $N.O_5$+3H.O.). The double salt, which forms less frequently, is in yellow plates, and has the formula (Hg. Ad. . $N.O_5$+3Hg.O.)+(H.Ad. . $N.O_5$. H.O.).

These double salts may also be generated by boiling oxide of mercury in solution of nitrate of ammonia. If the common basic nitrate of mercury be boiled in a solution of nitrate of ammonia, this is decomposed; the ammonia being employed in forming amidide of mercury, and the nitric acid being set free, as may be recognised by litmus.

The subsulphate of mercury, Hg_2O. . $S.O_3$, acted on by water of ammonia, produces a black powder, the formula of which is Hg_2O. . $S.O_3$+Hg_2Ad.: it is easily decomposed.

By acting on a solution of subnitrate of mercury in water with ammonia added dilute, and in such quantities as to leave a portion of the mercurial salt undecomposed, a fine velvet black precipitate is obtained, known in pharmacy as *Hahnemann's soluble Mercury*. It is very easily decomposed by heat or by an excess of ammonia. In order to obtain it pure, the solution should be quite free from red oxide, and not more than three fourths of the whole quantity of mercury should be precipitated. When quite pure, I have found its formula to be H.Ad. . $N.O_5$+2Hg_2O., it being perfectly analogous to the common basic subnitrate H.O. . $N.O_5$+2Hg_2O., the oxide of hydrogen being replaced by the amidide.

The results with the other salts, both of the red and black oxide of mercury, are similar to those above described; but as none of them are specially important, I shall not occupy space with their description.

7. *Ammonia-Salts of Platinum.*

When protochloride of platinum is dissolved in muriatic acid, and an excess of ammonia added, a green precipitate is produced, composed of Pt.Cl.+H.Ad. It may be prepared in larger quantity by passing a current of sulphurous acid gas through a solution of bichloride of platinum until it assumes a deep brown colour, and then adding ammonia. By boiling this green substance in strong water of ammonia, it forms a white powder, the formula of which is Pt.Cl.+2H.Ad.

The action of ammonia on a solution of bichloride of platinum is very complex; it gives origin to a series of bodies, composed of bichloride, binoxide, and binamidide of platinum, in proportions which vary with the temperature and proportions used. The ultimate effect is the formation of a colourless solution, when the ammonia is boiling and in considerable excess, from which a white powder separates by cooling, or by the addition of alcohol. This powder, which consists of ($Pt.Cl_2$+$Pt.Ad_2$)+2H.Ad.+2 Aq., combines with acids, and generates a very remarkable series of double salts, discovered by Gros, who formed them differently, having obtained the nitric acid salt by heating the green substance Pt.Cl.+H.Ad. with nitric acid, and the other salts by double decomposition. Liebig proposed to consider, that in these salts there exists a compound radical, Pt.Cl. . N_2H_6, which combines with chlorine and with oxygen, and the oxide of which unites with acids. Thus the oxalate contains Pt.Cl. . N_2H_6O.+C_2O_3, &c. But as the gradual formation of this supposed oxide can be traced from the bichloride of platinum, we must admit it to contain a compound of bichloride and binamidide, similar, in many respects, to white precipitate, and we must look upon the salts formed by Gros as consisting of that compound united to ordinary ammoniacal salts, just as are the double ammonia-nitrates of mercury.

The formulæ of Gros's salts are upon my view:

($Pt.Cl_2$+$Pt.Ad_2$)+2(H.O. . H.Ad.), the base of the series.
($Pt.Cl_2$+$Pt.Ad_2$)+2(H.Cl. . H Ad.), the muriatic salt.
($Pt.Cl_2$+$Pt.Ad_2$)+2(H.O. . $N.O_5$. H.Ad.), the nitric salt.
($Pt.Cl_2$+$Pt.Ad_2$)+2(H.O. . $S.O_3$. H.Ad.), the sulphuric salt.
($Pt.Cl_2$+$Pt.Ad_2$)+2(H.O. . C_2O_3 . H.Ad.), the oxalic salt.

The action of ammonia on biniodide of platinum is more simple; a deep red powder is formed, which has the formula $Pt.I_2+Pt.Ad_2+4$ Aq.

Our knowledge of the action of ammonia on the oxygen salts of platinum is yet too inexact to justify me in bringing forward here the statements that have been made concerning the results.

By the action of ammonia on perchloride of gold, an olive-brown powder is produced, which fulminates when rubbed. It is decomposed by water, and its real formula has not yet been established.

Products of the Action of Ammonia on the Anhydrous Acids.

When chloro-sulphurous acid, $S.O_2Cl.$, is exposed to dry ammonia, it is converted into a white saline mass, which is a mixture of sal ammoniac and *sulph-amide*, $S.O_2Cl.$ and 2Ad.H. giving $S.O_2Ad.$ and H.Cl.+H.Ad. The former, which consists of amidogene united to sulphurous acid, is soluble in water, and may be obtained crystallized, but when boiled with water it is changed into common sulphate of ammonia, 2H.O. and $S.O_2Ad.$ giving $S.O_3+Ad.H.\ .\ H.O.$

When dry sulphurous acid and ammonia gases are mixed, they combine to form a reddish substance, which is decomposed by water; there appear to be two proportions, giving the bodies $S.O_2\ .\ H.Ad.$ and $2S.O_2\ .\ H.Ad.$

Dry sulphuric acid unites with dry ammonia in two proportions, forming $S.O_3\ .\ H.Ad.$ and $2S.O_3\ .\ H.Ad.$ I consider these compounds as corresponding to the English and German hydrates of sulphuric acid, the ammonia playing the part of water. A solution of these bodies is not at first precipitated by barytes, but gradually becomes changed into ordinary sulphate of ammonia.

It was supposed that the chloro-carbonic acid, C.O.Cl., combined directly with ammonia, but Regnault has found that decomposition occurs, and that sal ammoniac and amidide of carbonic oxide result. This body, which he terms *carb-amide*, C.O.Ad., is white, soluble in water, is not deliquescent, and resists the action of alkalies and acids, unless they be very concentrated.

Of the Common Ammoniacal Salts.

From the great number of classes of compounds described in the preceding sections, it is evident that ammonia enters into combination with acids and with bases, with haloid and with oxygen salts, in such manner as assimilates it fully to the oxide and chloride of hydrogen in its action, but removes it totally from all analogy with the alkalies, to which it, in other points of view, strictly belongs. For the ordinary salts of ammonia, of which the description now comes, are isomorphous with the corresponding salts of potash, and the strong basic characters of the solution of ammonia had given to it, from the earliest times, the name of the *Volatile*, or the *Animal Alkali.* The characteristic distinction is, that in all cases where it acts as an alkali, ammonia is associated with water: it is not Ad.H., which is the alkali, but Ad.H.+H.O., or, rather, $N.H_4O.$, the element which replaces potassium in the isomorphous salts being *sub-amidide of Hydrogen*, $Ad.H_2$, or $N.H_4$.

At the time when Mitscherlich showed the isomorphism of the potash and ammonia salts, nothing was known of the true constitution of ammonia or of amidogene; and, in order to explain the necessity of the presence of water, a very ingenious theory was proposed by Berzelius and Ampere. It was, to consider that these ammoniacal salts do not contain ammonia at all, but another compound of nitrogen and hydrogen, $N.H_4$, which is metallic, and resembles potassium in all general characters, and for which the name *Ammonium* was proposed. This view squared accurately with experiment, as in every oxygen salt of ammonia there is just so much water as may form with the ammonia *Oxide of Ammonium*, $N.H_4O.$; and in every haloid salt, the electro-negative body is combined

with as much hydrogen as may convert the ammonia into the compound metal; thus $N.H_3 . H.O.+S.O_3$ and $N.H_3+H.Cl.$ would give $N.H_4O.+S.O_3$ and $N.H_4Cl.$ Not merely was this theory consonant to numbers, but experiment gave very good reason to believe in the real existence of this compound metal, by the remarkable properties of the *ammoniacal amalgam.*

When a globule of mercury, immersed in water of ammonia, is made the negative pole of a galvanic battery, it increases fifty times in volume, becomes semi-fluid and covered with warty excrescences, and finally becomes so light as to float on water. No hydrogen is evolved from its surface, but oxygen is copiously given off from the positive electrode. If the current be interrupted, a copious disengagement of hydrogen occurs from this metallic sponge, which also gives off ammonia, and it soon falls back to its original appearance. By cold, this decomposition may be retarded; the pasty mass may be removed from the liquor, and is found to crystallize in cubes at a cold of 0°; and if decomposed when dry over mercury, it evolves ammonia and hydrogen, by volume in the proportion of 2 : 1. This indicates that the mercury is therein combined with a body which consists of $N.H_4$, and as the mercury retains its lustre, the compound formed is properly an alloy, and the body $N.H_4$ is of a metallic nature. It may be the metal *Ammonium*, almost perfectly isolated. All these phenomena may be observed by dissolving one grain of potassium in 100 grains of mercury, and dropping the globule into a glass containing strong solution of sal ammoniac. By the action of $K.Hg.$ on $N.H_4Cl.$, there are produced $K.Cl.$ and $Hg.N.H_4$; the globule of mercury swells up rapidly, and the amalgam is sufficiently permanent to be easily examined.

I have no doubt there is thus obtained a substance possessing some metallic characters, and consisting of ammonia and hydrogen; in fact, *subamidide of Hydrogen*, $Ad.H_2$; but whether the water which is found in the common ammoniacal salts exists therein as such, or whether these salts contain true oxide of ammonium, is not thus decided. In fact, among the metallic compounds of ammonia already examined, we have found bodies every way similar to the ordinary salts of ammonia, except that a part of the hydrogen is replaced by a metal. Thus, if we compare sal ammoniac with other similar bodies, as in the following formulæ,

1. $Cl.N.H_4$,	5. $Cl.N..H_3Ni.$,
2. $Cl.N..H_3Cu.$,	6. $Cl.N..H_3Hg.$,
3. $Cl.N..H_3Zn.$,	7. $Cl.N..H_2Hg_2$,
4. $Cl.N..H_3Pd.$,	8. $Cl.N..H_2Pt_2$,

and find them all produced by the action of ammonia on a chloride of a metal, just as sal ammoniac is formed by the action of ammonia on chloride of hydrogen, we must admit their similarity of constitution; and if we say that in No. 1, $N.H_4$ forms a compound metal, we must consider all the others as chlorides of compound radicals also. Still more, the connexion is so perfect from these bodies to such as resemble the yellow powder, $Hg.Cl.+2Hg.O.+Hg.Ad.$, and from that to the oxychloride, $Hg.Cl.+3Hg.O.$, that if we insist on assuming the compound metal ammonium to exist ready formed in the salts of ammonia, we must lay down as a gen-

eral principle that all basic salts are salts of compound metals, which could not be tolerated in an exact science for a moment. At the same time, therefore, that I consider the ammoniacal amalgam to contain ammonium, I believe it to be formed only at the time, and that the ordinary salts of ammonia contain ammonia and water, the latter being united as the constitutional water is in the magnesian sulphates, but more intimately. Thus, sulphate of ammonia, $S.O_3+Ad.H..H.O.$, I consider to resemble the bihydrated sulphuric acid, $S.O_3+H.O..H.O.$ In both cases an atom of water may be replaced by an oxide of the magnesian class.

It will be necessary only to notice the more important of the ordinary salts of ammonia.

Muriate of Ammonia. Sal Ammoniac.—$Cl.H_2Ad.$ Eq. 666·8 or 53·5. This salt, formerly derived from Africa, is now manufactured on the large scale from the ammoniacal liquor obtained in the destructive distillation of horns, bones, coals, and such other organic matters as contain nitrogen. Those liquors which contain ammonia, combined principally with carbonic acid and sulphuretted hydrogen, are decomposed by means of muriatic acid added in slight excess. By evaporation to a pellicle and cooling, the sal ammoniac is obtained in small crystals, deeply coloured with tarry matter. They are purified by re-crystallization, and finally placed in cast iron pots, set in a furnace, lined with fire-tiles, and fitted with leaden heads, into which the sal ammoniac is sublimed. The temperature is so managed that the sublimed salt forms a coherent, hemispherical mass, often weighing 100 lbs., and when pure should be perfectly free from yellow stains, and nearly transparent. If muriatic acid be dear, the ammoniacal liquor may be neutralized by sulphuric acid; sulphate of ammonia is formed, which is decomposed by the addition of common salt, and the sulphate of soda and sal ammoniac separated by crystallization.

Sal ammoniac is very soluble in water; it crystallizes both by sublimation and solution, in cubes and octohedrons; it is slightly deliquescent, and is soluble in alcohol; it volatilizes below a red heat. When heated with lime or potash, it yields ammonia, as described in p. 499. It consists of an equivalent of each element, its formula being $H.Cl..H.Ad.$ It may be formed by their direct combination. When equal volumes of dry muriatic acid gas and ammonia are mixed together, the two gases disappear, and a snow-white powder of sal ammoniac results. Hence arise the white fumes when a rod dipped in water of ammonia is brought where chlorine or muriatic acid gas is evolved, or when a rod dipped in muriatic acid is brought to where ammonia is escaping. It thus renders these bodies the means of detecting each other.

Sal ammoniac is remarkable for the number of double salts which it produces, and of which some deserve notice.

With chloride of magnesium, it forms the anhydrous salt $Ad.H_2Cl.+Mg.Cl.$, which is used in preparing metallic magnesium.

With perchloride of iron, it crystallizes in fine red octohedrons, $Fe_2Cl_3+3(Ad.H_2Cl.)$. When these are heated, sal ammoniac sublimes, coloured by some chloride of iron, and forms thus the *Flores Martiales*.

The double salts formed with the chlorides of copper, zinc, and nickel, crystallize in cubes. They are all composed like that of copper, which is $Cu.Cl.+Ad.H_2Cl.+2\,Aq.$

Corrosive sublimate unites in two proportions with sal ammoniac. The first salt, of which the formula is $Hg.Cl.+Ad.H_2Cl.+Aq.$, is very soluble in water, and crystallizes in flat rhomboidal tables, which effloresce when exposed to the air. This is the *Sal Alembroth* of the older chemists. The second salt crystallizes in rhomboidal prisms, which sublime unchanged, and have the formula $2Hg.Cl.+Ad.H_2Cl.$ It is by the formation of these salts that corrosive sublimate becomes so easily soluble in a solution of sal ammoniac.

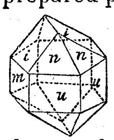
Sal ammoniac and bichloride of platinum form a double salt, whose formula is $Pt.Cl_2+Ad.H_2Cl.$ It precipitates as a bright yellow powder when solutions of its constituents are mixed, and especially if alcohol be added, in which it is quite insoluble. It is but very sparingly soluble in water, but more so in boiling water, from which it crystallizes in orange-red octohedrons. When ignited, it leaves behind metallic platinum in the form of a light sponge. It is of use in preparing spongy platina, and in the detection of ammonia.

With chloride of gold, sal ammoniac forms a double salt, which crystallizes in orange-red cubes, having the formula $Au.Cl_3+Ad.H_2Cl.+2\,Aq.$

The hydrobromate and hydriodate of ammonia do not require notice. They resemble the sal ammoniac in all important characters, and combine with the metallic bromides and iodides to form similar double salts.

Hydrosulphuret of Ammonia.—When sulphuretted hydrogen and ammonia gases are mixed in equal volumes, in a vessel cooled by ice, they combine, forming colourless needles, which evaporate at ordinary temperatures. The formula of this compound is $S.H.+H.Ad.$, or $S.N.H_4$, analogous to protosulphuret of potassium, S.K. Like that, it combines with as much more sulphuret of hydrogen, forming a volatile crystalline compound, $Ad.H_2S.+H.S.$ This *bihydrosulphuret of Ammonia* is formed also when sulphuretted hydrogen is passed into water of ammonia, as long as it is absorbed. For each atom of ammonia present, two atoms of sulphuretted hydrogen are taken up. By exposure to the air, this solution becomes yellow, owing to the absorption of oxygen and the liberation of sulphur. It is capable of dissolving a large quantity of sulphur, forming compounds analogous to the higher sulphurets of potassium. This hydrosulphuret of ammonia is of great importance in the detection of the metals, from the formation of metallic sulphurets. It is a sulphur base, and forms salts with the sulphur acids, analogous to those formed by sulphuret of potassium.

Sulphate of Ammonia.—$Ad.H_2\,.\,O.S.O_3+Aq.$ This salt is formed on the large scale in the manufacture of sal ammoniac; it may be prepared pure by neutralizing water of ammonia by sulphuric acid; it



crystallizes in flat rhomboidal prisms, as in the figure, or in macles, isomorphous with the crystals of sulphate of potash. It is very soluble in water, but insoluble in alcohol; when heated, it gives off water, ammonia, and azote, and sulphite of ammonia sublimes. It combines with the sulphates of copper, zinc, iron, alumina, &c., forming double salts exactly analogous to those formed by sulphate of potash. With oil of vitriol it unites to form *bisulphate of Ammonia*, which is deliquescent and soluble in alcohol.

Nitrate of Ammonia, $Ad.H_2O.\,.\,N.O_5$, is formed by neutralizing nitric acid by ammonia. It crystallizes in striated hexagonal prisms, isomorphous with nitre, of a bitter saline taste; they are deliquescent and very soluble in water. When heated, they fuse at 230°, and at about 460° are rapidly decomposed into nitrous oxide and water, as described p. 272. By the presence of a large excess of sulphuric acid, this action takes place at much lower temperatures.

When heated with combustible bodies, it deflagrates with extreme violence.

Phosphates of Ammonia.—The tribasic phosphoric acid forms with ammonia two salts; the first, whose formula is $(P.O_5+Ad.H_2O.+H.O.)+Aq.$, is prepared by adding the acid in excess to water of ammonia; it crystallizes in rhombic prisms, which are very soluble in water. Their reaction to test-paper is strongly acid. If the ammonia be added in excess, a salt crystallizes, possessing nearly the same characters, except that its reaction is alkaline, and its formula $P.O_5+2(Ad.H_2O.)+H.O.$ Both of these salts yield, by ignition, phosphoric acid.

Ammoniaco-Magnesian Phosphate.—When a solution of a salt of magnesia is added to any soluble phosphate, and the liquor rendered alkaline by ammonia, a crystalline precipitate is formed, which is soluble in acids, sparingly soluble in water, but insoluble in alkaline liquors. Its formula is $P.O_5+(Ad.H_2O.+2Mg.O.)+12$ Aq. Its formation is often of use for the detection of magnesia, and it is occasionally generated in urine by the action of ammonia, produced by the spontaneous decomposition of urea upon the soluble phosphates of magnesia which it contains. It then constitutes a common variety of calculus.

Phosphate of Ammonia and Soda.—This salt, of which the formula is $P.O_5+(Ad.H_2O.+Na.O.+H.O.)+8$ Aq., is easily produced by mixing together, in solution, six parts of common phosphate of soda and one of sal ammoniac. On cooling, it crystallizes in large prisms, which effloresce in the air. When heated, it gives monobasic phosphate of soda and free phosphoric acid, as a source of which it is much used in blowpipe experiments, under the name of *Microcosmic Salt.* It is found in all the animal fluids.

Carbonates of Ammonia.—The salt which, under this name, is used for medicinal purposes, is prepared by mixing together one part of sal ammoniac with two of powdered chalk, and exposing the mixture in an earthen pot to a heat below redness. These bodies reacting, produce chloride of calcium and carbonate of ammonia, which sublimes, and is condensed as a crystalline semi-transparent mass, in a dome-shaped receiver, which is fastened on the subliming pot. By right, this should be a neutral salt, $Ad.H_2Cl.$ and $Ca.O..C.O_2$ giving $Ca.Cl.$ and $Ad.H_2O..C.O_2$; but a quantity of ammonia and water is given off, and the sublimed salt was considered to be a sesquicarbonate, consisting of $2(Ad.H_2O.)+3C.O_2$, until Scanlan showed that it was a mixture of two different salts, which may be separated by water. Rose has recently thoroughly examined the carbonates of ammonia, of which there are a great number, but only four sufficiently important to be noticed here.

The proper neutral carbonate of ammonia, $Ad.H_2O..C.O_2$, does not exist except in combination, but its compounds are very numerous; it forms,

1st. With carbonate of water, the ordinary *bicarbonate of Ammonia*, $Ad.H_2O..C.O.+H.O..C.O_2$. This is prepared by washing the commercial sesquicarbonate with cold water or alcohol, when it remains behind as a skeleton of crystalline grains, which are isomorphous with bicarbonate of potash. It evaporates spontaneously, with a

weak odour of ammonia. Its solution reacts feebly alkaline. By pouring on the commercial sesquicarbonate as much boiling water as dissolves it, and letting the solution cool in a close bottle, so that no carbonic acid can escape, this salt may be obtained in large rhomboidal crystals, which contain one and a half atoms of water.

2d. The substance which is dissolved out of the sublimed mass of sesquicarbonate by alcohol is identical with that formed by the union of dry carbonic acid and ammonia. Its formula is therefore $Ad.H..C.O_2$, and the ordinary sesquicarbonate is a mechanical mixture of it with the bicarbonate.

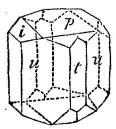
When the sublimed sesquicarbonate is distilled at a moderate heat in a retort, it abandons carbonic acid, and two salts, differing in volatility, are condensed in the neck. The more volatile consists of $Ad.H_2O..C.O_2+H.Ad..C.O_2$, being a compound of neutral carbonate with dry carbonate, or a bicarbonate in which the basic oxide of hydrogen is replaced by amidide of hydrogen, the two double salts,

$Ad.H_2O..C.O_2+H.O..C.O_2$, water-bicarbonate of ammonia,
$Ad.H_2O..C.O_2+H.Ad..C.O_2$, ammonia-bicarbonate of ammonia,

being precisely equivalent in composition. The less volatile product is of very complex composition; its formula is $4(Ad.H_2O.)+5C.O_2$, or it consists of an atom of neutral carbonate united to an atom of each of the different bicarbonates, thus:

$$\left.\begin{array}{l} Ad.H_2O..C.O_2 \\ Ad.H_2O..C.O_2+H.O..C.O_2 \\ Ad.H_2O..C.O_2+H.Ad.Co_2 \end{array}\right\} = 4(Ad.H_2O.)+5C.O_2.$$

Oxalate of Ammonia, $Ad.H_2O..C_2O_3$, may be prepared by neutralizing oxalic acid by water of ammonia; it crystallizes in right rhombic prisms, as in the figure, where *p*, *u*, *u* are primary, and *i*, *t* secondary planes. These crystals contain an atom of water, which they lose by efflorescence in dry air. When heated, it is completely decomposed, water being evolved, and *oxamide* subliming, $Ad.H_2O..C_2O_3$ producing $2H.O.$ and $Ad.C_2O_2$. This neutral oxalate of ammonia combines with oxalic acid, forming a binoxalate and a quadroxalate like those of potash.



The *oxamide* may also be prepared by acting on oxalic ether with water of ammonia, or by dissolving oxalic acid in a mixture of equal volumes of oil of vitriol and alcohol, and adding ammonia in excess. It is a light white powder, tasteless and insoluble in water; it is decomposed by acids and by strong bases, in contact with water, oxalic acid and ammonia being regenerated. Its discovery by Dumas laid the foundation of our present knowledge of the nature of ammonia, by leading him to the idea of the probable existence of amidogene.

CHAPTER XIX.

OF CYANOGEN AND ITS COMPOUNDS, AND OF THE BODIES DERIVED FROM IT

THERE is no class of organic bodies of which our knowledge is more extensive and exact, than those which have cyanogen as their basis. The powerful affinities which this radical exerts, the simplicity of its constitution, and, above all, our being able to prepare it in an isolated form, and to generate its compounds directly from it, as we could those of a truly simple body, render its history the most advanced portion of organic chemistry, and that to which the analogy of mineral bodies and the theory of compound radicals is most undeniably applicable.

Cyanogen does not exist in nature ready formed; the kernels of peaches, plums, bitter almonds, &c., and the leaves of the cherry-laurel, yield, by simple distillation, abundance of prussic acid (cyanide of hydrogen), but this is only then produced by the decomposition of other substances containing nitrogen.

Cyanogen may, however, be formed abundantly, and in a simple manner, by bringing its elements together at a high temperature, in contact with substances with which it may unite. Thus, when any organic substance containing nitrogen is calcined with potash, the nascent carbon and nitrogen unite, and cyanide of potassium is formed; even with pure charcoal this occurs, nitrogen being derived from the air; and Mr. Fownes has shown, that when a mixture of pure charcoal and potash is ignited in a tube, and a current of pure nitrogen passed through it, this is absorbed, and carbonic oxide gas being given off, cyanide of potassium is produced, 3C. with K.O. and N. giving C.O. and $C_2N.K.$ By the action of ammonia, also, on ignited charcoal, cyanogen is formed in abundance; it combines with hydrogen and the excess of ammonia, and produces prussiate of ammonia. In this case 2C. and $2N.H_3$ produce $C_2H.+N.H_3$, and H_2 become free. It is by virtue of these processes that cyanogen is produced for its various applications in the arts; but, as I shall return to them in detail, I shall now only consider farther the mode of obtaining it free and pure.

Cyanide of silver, or cyanide of mercury, of which the preparation will be described hereafter, is to be introduced into a small glass retort, and heated to just below redness; a gas is given off, which must be collected over the mercurial trough; the cyanide of silver separates simply into metal and cyanogen; but when cyanide of mercury is used, a brown powder appears, the quantity of which is less as the temperature of decomposition has been lower. The gas which comes over is, however, cyanogen completely pure.

Its properties are very marked. It is colourless, of a sharp smell, which irritates the eyes. Its sp. gr. is 1819. If a quantity of cyanide of silver be sealed up in a strong tube, bent as in the figure, and then heated at one end, *a*, the cyanogen is condensed by a press-

ure of about four atmospheres, and collects at the other end, *b*, as a colourless liquid. It is combustible, burning with a beautiful rose-coloured flame, and producing two volumes of carbonic acid and one of nitrogen. It is constituted, therefore, of equal volumes of carbon vapour and nitrogen, the two volumes being condensed to one; hence $843+976=1819$ is its sp. gr. It dissolves abundantly in alcohol and water, but these solutions soon undergo very complex decompositions, the liquor being found to contain carbonic acid, prussic acid, ammonia, urea, and oxalic acid, besides a brown insoluble matter. A similar decomposition is produced much more rapidly by contact with water of ammonia. The composition of this brown matter appears to be $C_4N_2 . H.O.$ It dissolves in alkalies, and gives precipitates with the metallic salts; it has been termed hence *Azulmic Acid.* When heated, it gives off water, and leaves a deep brown powder, of the same composition as cyanogen, and which has been termed *Paracyanogen.* This may be also formed by heating cyanide of mercury very strongly. It dissolves in hot nitric acid, and the solution gives, with water, a yellow precipitate, which combines with bases, and has been termed *Paracyanic Acid.* By strong ignition, paracyanogen evolves nitrogen, and a very dense carbon remains.

Cyanogen combines directly with hydrogen and with the metals, but its oxygen combinations require to be indirectly formed; there are three compounds of cyanogen and oxygen, which are all acids, and are polymeric bodies. It unites also with sulphur, and its compounds have a remarkable tendency to form double and triple combinations.

The formula of cyanogen is indifferently written $C_2N.$ or Cy. Its equivalent number is 328·6 or 26·05.

SECTION I.

NON-METALLIC COMPOUNDS OF CYANOGEN.

Compounds of Cyanogen and Oxygen.

Cyanic Acid—Cy.O.; Eq. 428·6 or 34·05—is very easily obtained in combination, by calcining the cyanide of potassium in contact with the air, at a temperature below redness, in which case oxygen is directly absorbed; or by heating the cyanide with nitre, or with peroxide of manganese, which yield the oxygen required. For this purpose the yellow prussiate of potash of commerce may be employed, as the cyanide of iron which it contains is totally decomposed, and the cyanide of potassium then acts as if it were completely pure. The cyanic acid cannot, however, be isolated from these salts by a stronger acid, as it then rapidly changes into bicarbonate of ammonia, uniting with the elements of three atoms of water; thus $C_2N.O.$ and $3H.O.$ produce $N.H_3$ and $2C.O_2$.

The cyanic acid can be obtained free only by distilling the cyanuric acid, $Cy_3O_3+3H.O.$, which then transforms itself into the hydrated cyanic acid, $Cy.O.+H.O.$, and is to be collected in a receiver surrounded with snow. It is a colourless liquid, of a very pun-

gent odour, cauterizes the skin, and, when mixed with water, is decomposed as above stated. When preserved in its most concentrated form, it soon transforms itself into a white mass, like porcelain, of the same composition, $C_2N..H.O_2$, which has been termed *Cyanamelide.* This body is insoluble in water, but by heat is transformed back again into hydrated cyanic acid, and by strong acids is resolved into carbonate of ammonia.

Cyanic acid does not exist in the anhydrous state.

The cyanic acid forms but one series of salts, being monobasic; those of the alkalies are soluble; the others are white insoluble powders.

Cyanate of Potash.—Cy.O..K.O. The yellow prussiate of potash of commerce, being roasted in an earthen dish, absorbs oxygen, and the cyanide of potassium is converted into cyanate of potash. When the mass becomes adhesive from the fusion of the product, it is to be digested with alcohol, from which the pure cyanate crystallizes, on cooling, in rhombic tables like chlorate of potash. In contact with water this salt is rapidly decomposed, ammonia being evolved, and carbonate of potash formed. If dry cyanate of potash and dry crystals of oxalic acid be rubbed together in a mortar, oxalate of potash is formed, and the cyanic acid changes into cyanamelide.

Cyanic Acid and Ammonia.—If hydrated cyanic acid be placed in contact with dry ammonia, they combine, and form a white, woolly mass, which dissolves in water, and acts as an ordinary cyanate. It appears to contain $Cy.O.+H.O.+2N.H_3$. If it be gently heated it gives off ammonia, and is transformed into an important substance, *Urea*, which, though thus capable of being artificially produced, will be specially described as a product of the organization, in another chapter. Whenever we attempt to form the neutral cyanate of ammonia, $Cy.O..N.H_3.H.O.$, urea is produced; thus, by acting on cyanate of silver with muriate of ammonia, or by mixing solutions of sulphate of ammonia and cyanate of potash. But still we cannot consider urea to be merely cyanate of ammonia, to which it bears the same relation that cyanamelide does to hydrated cyanic acid.

Fulminic Acid.—$Cy_2O_2+2H.O.$ This acid, which has attracted much attention from the detonating properties of its salts, is prepared by the action of nitric acid on alcohol, in presence of oxide of mercury or silver. The reaction is very complex; a crowd of products of the oxidation of the alcohol being evolved, as aldehyd, formic, acetic, and oxalic acid, &c. If the action were limited to the essential conditions, it would probably consist in two equivalents of alcohol and two of nitric acid, producing one of acetic acid, one of fulminic acid, and eight of water; thus $2N.O_5$ and $2(C_4H_6O_2)$ give $C_4H_4O_4$ and $C_4N_2O_2$, besides $8H.O$.

The fulminic acid cannot be obtained in an isolated form; when we attempt to separate it from bases, it is instantly decomposed. Thus, if fulminate of silver be acted on by dilute muriatic acid, chloride of silver, and a peculiar acid containing chlorine and cyanogen, are produced. The fulminic acid is bibasic, and forms two series of salts, of which the neutral contains two equivalents of fixed base, the acid salts containing one of fixed base and one of water

Fulminate of Silver.—$Cy_2O_2+2Ag.O$. It is prepared by dissolving silver in ten parts of nitric acid, specific gravity 1·35, and pouring the solution, when cold, into twenty parts of rectified spirits of wine. The mixture is to be gently heated till it begins to boil, and then left to cool slowly. The fulminate of silver is deposited in fine silky crystals, snow-white, and equal in weight to the silver employed. It is very sparingly soluble in cold water. It detonates with the slightest shock, or by contact with sulphuric acid. When acted on by a caustic alkali, as potash, half of the silver separates as oxide, and a salt is formed, $Cy_2O_2+K\ O..Ag.O$. If it be dissolved in warm dilute nitric acid, half of the silver is also removed and replaced by water, and on cooling, the acid fulminate of silver, $Cy_2O_2+H.O..Ag.O.$, crystallizes out. This explodes more readily than the first salt, by friction, and by contact with oil of vitriol or chlorine gas.

By digesting these fulminates of silver with metallic zinc or copper, fulminates of these metals with two atoms of oxide are obtained; and by acting on these salts with an alkali or barytes, salts with two different bases may be formed. In no case, however, can a fulminate containing two atoms of an alkaline base be produced. All these salts possess detonating properties more or less violent.

Fulminate of the Suboxide of Mercury.—$Cy_2O_2+2Hg_2O$. This, the most important salt of fulminic acid, is prepared by dissolving mercury in nitric acid, and treating it by alcohol, as in preparing fulminate of silver. As the solution cools, some metallic mercury precipitates, and the fulminate of the suboxide is deposited in hard, opaque, white crystals, generally very minute. It is to be washed and redissolved in boiling water, and crystallizes then in fine silky needles. This salt detonates violently when struck between two hard bodies. It is extensively used in the manufacture of the percussion caps used for firearms. As a great quantity of alcohol is wasted in this process, it was proposed to carry on the action in close vessels, and condense the spirit, which, however, was found to be unfit for any but the same use, from containing a large quantity of prussic acid.

Cyanuric Acid.—$Cy_3O_3+3H.O$.

This acid is produced under a variety of circumstances where the elements of cyanic acid become free. Thus, if the solid chloride of cyanogen be treated with water, Cy.Cl. and H.O. produce H.Cl. and Cy.O., but this transforms itself immediately into cyanuric acid. It is formed abundantly, as a white sublimate, in the dry distillation of uric acid, and may be very simply produced by heating urea a little above its point of fusion in a glass retort; ammonia is given off, and the urea changes into a dry, gray mass, which is to be dissolved in strong sulphuric acid, and treated with nitric acid, added in small quantities, until it becomes quite colourless. Being then diluted with its own weight of water, the liquor yields crystals of cyanuric acid on cooling. It is evident that three atoms of urea, $3(C_2H_4.N_2O_2)$, contain the elements of three atoms of ammonia and one of cyanuric acid, $C_6N_3O_3+3H.O$.

By means of a substance which will be hereafter noticed, termed

Melam, cyanuric acid may be formed simply and in quantity. The details of the process will be given when describing the properties of that body.

Cyanuric acid is colourless and nearly tasteless, possessing a very slight acid reaction. It crystallizes in oblique rhombic prisms, which have the formula $Cy_3O_3+3H.O.+4$ Aq. By a moderate heat, the 4 Aq. are expelled, and when more strongly heated, the dry acid changes into hydrated cyanic acid. This acid, being tribasic, forms three distinct classes of salts, which differ as the quantity of fixed base is one, or two, or three atoms. If any of these salts be acted on by a stronger acid, the cyanuric acid is completely liberated.

Cyanide of Hydrogen. Hydrocyanic Acid. Prussic Acid.

This remarkable substance may be formed by the direct combination of hydrogen and cyanogen. It exists in the water distilled from bitter almonds, or from the leaves of the cherry-laurel, being produced by the decomposition of a peculiar substance, *Amygdaline*, which those plants contain. For the purposes of medicine and chemistry, it is prepared by indirect processes of many kinds. Thus, if formiate of ammonia ($C_2H.O_3+N.H_4O.$) be passed in vapour through a red-hot porcelain tube, it is totally converted into prussic acid and water, $C_2N.H.$ and $4H.O.$ Also, by passing ammonia over red-hot charcoal, hydrocyanate of ammonia is formed in such quantity that prussic acid may be economically prepared from it. If cyanide of silver be decomposed by muriatic acid, chloride of silver and cyanide of hydrogen are produced ($Ag.Cy.$ and $H.Cl.$ giving $Ag.Cl.$ and $H.Cy.$); and by sulphuret of hydrogen, cyanide of mercury gives sulphuret of mercury and prussic acid. For its preparation on the large scale, however, the substance used is the yellow prussiate of potash of commerce.

This salt, the preparation of which will be hereafter described, consists of cyanide of iron united to cyanide of potassium; by the action of sulphuric acid, three fourths of the latter are decomposed, bisulphate of potash being formed, and prussic acid liberated, $2(S.O_3+H.O.)$ and $Cy.K.$ giving $(K.O.\,.\,S.O_3+H.O.\,.\,S.O_3)$ and $Cy.H.$ The cyanide of iron remains still combined with the other fourth of the cyanide of potassium, forming a compound first described by Mr. Everitt. The prussic acid thus produced contains, therefore, one half of the cyanogen which existed in the salt employed. The precise decomposition is, that two equivalents of the yellow ferroprussiate of potash, $2(Fe.Cy.+2K.Cy.)$, acted on by six atoms of oil of vitriol, $6(S.O_3+H\,O.)$, produce three atoms of bisulphate of potash, $3(H.O.\,.\,S.O_3+K.O.\,.\,S.O_3)$, and three atoms of prussic acid, $3H.Cy.$; there remains then an atom of Everitt's salt, $2(Fe.Cy.+K.Cy.)$, which, when first formed, is yellow, but by rapidly absorbing oxygen it becomes greenish, and, abandoning its cyanide of potassium, is finally converted into basic Prussian blue.

The mode of conducting the process depends on the degree of strength at which the prussic acid is required. To obtain the anhydrous acid, three parts of yellow prussiate of potash, in fine powder, are to be decomposed by a mixture of two parts of oil of vitriol and two of water, in a small retort, at a very gentle heat, and

the product collected in a receiver, surrounded by ice, and containing some fragments of recently-fused chloride of calcium, by which any traces of water which come over are absorbed. The process originally employed by Gay Lussac consists in decomposing cyanide of mercury by strong muriatic acid, and passing the vapour through a long tube, of which the half next the retort contains small fragments of marble, and the other half fragments of recently-fused chloride of calcium; any muriatic acid vapour is arrested by the former, and the prussic acid is rendered anhydrous by the latter; the vapour is then condensed in a receiver, surrounded by ice.

Pure prussic acid is a colourless liquid; its specific gravity at 67° is 0·6969; at 5° Fah. it congeals into a mass of fibrous crystals, and at 80° boils. In consequence of this great volatility, if a drop of it be suspended from a glass rod, one part of it will be solidified by the cold, produced by the rapid evaporation of another portion. The density of its vapour is 943·9, consisting of equal volumes of cyanogen and hydrogen, united without condensation, as $(1819{\cdot}0+68{\cdot}8)\div 2=943{\cdot}9$. It reddens litmus paper feebly, and the tint disappears by heat. Its odour is extremely suffocating and pungent, and resembles that of bitter almonds. Its taste is bitter and acrid. It is combustible, burning with a bright white flame. Being a poison of intense activity, the greatest care should be used in manipulating with it in this concentrated form.

Anhydrous prussic acid decomposes rapidly, especially if exposed to light. It forms ammonia, and a brown substance, probably the same as that produced from a solution of cyanogen in water, and termed *Azulmic Acid*, as noticed p. 514, but of which the composition is not well known. By contact with a strong acid, prussic acid assimilates the elements of three atoms of water, and produces formic acid and ammonia ($C_2N.H.$ and $3H.O.$ giving $C_2H.O_3$ and $N.H_3$). Hence, in the preparation of prussic acid, an excess of any mineral acid should be avoided. With chlorine, prussic acid forms muriatic acid and chloride of cyanogen, and with iodine it acts similarly.

For medicinal use, the prussic acid is prepared in a very dilute condition. The directions sometimes given in pharmacopœias to distil over an acid of a specific strength, are, in practice, very difficult to execute, and might give rise to serious errors. The proper method is to prepare an acid stronger than that required; then, to ascertain by accurate analysis its strength, and dilute it with distilled water until it be brought exactly to the degree required. This process is carried on in the manufacturing laboratory of the Apothecaries' Hall of Ireland as follows: 1 lb. of crystallized yellow prussiate of potash, in fine powder, is placed in a capacious retort, and 2 lbs. of water poured on it; to this is added a mixture of 12 ozs. of oil of vitriol and 2 lbs. of water, previously suffered to cool. These materials are well agitated, and allowed to digest for three or four hours, and then between 2 and 3 lbs. of dilute acid are distilled over into a receiver containing already 1 lb. of distilled water; there are obtained thus 3 or 4 lbs. of an acid containing from 6 to 8 per cent. of real acid. 200 grs. of this are weighed and decomposed by an excess of nitrate of silver; the cyanide of silver pre-

cipitated is carefully collected, washed, and dried. Being then weighed, the exact per centage of acid present is found by calculation, and the necessary quantity of water is added, so as to bring it to the standard strength of the Dublin pharmacopœia, which is that of 1·6 per cent. of real acid, and specific gravity of 0·998.

As an example of this process, let us suppose that the 200 grs. of distilled acid gave, with nitrate of silver, 74 grs. of cyanide; as this contains 14·95 of cyanogen, the 200 grs. contained 15·53 of real acid, or 7·76 per cent.; now, to reduce this to the Dublin standard, divide 7·76 by 1·6, which gives 4·85; indicating that by adding 3·85 lbs. of distilled water to each pound of acid, the mixture will have accurately the strength directed by the pharmacopœia. Some of this calculation may be spared by considering the cyanide of silver to be equivalent to one fifth of its weight of real prussic acid; the quantity per cent. in the supposed example should then be one tenth of the weight of cyanide of silver obtained from the 200 grs., that is, 7·4 per cent.; and the water necessary to bring it to the Dublin standard should be 3·63 times its weight. The error introduced by this simplification is not sensible, being but 0·002 per cent.

The strength of the prussic acid directed by the British pharmacopœias differs very much: that prescribed by the London College contains about 2 per cent. of real acid; that of the Edinburgh College contains about 4 per cent.; while the Dublin strength is but 1·5 or 1·6 of real acid per cent. This should be carefully attended to in practice.

A method has been proposed for determining the value of prussic acid, by digesting it on a known quantity of red oxide of mercury; when the prussic acid has saturated itself with the oxide, what remains is to be washed, dried, and weighed. Now, as 116·4 of oxide of mercury is converted into cyanide by 27·1 of prussic acid, which proportion is nearly 4 to 1, the quantity of prussic acid is pretty correctly one fourth of the weight of the oxide of mercury dissolved. But as cyanide of mercury may combine with an excess of oxide, and as the quantity thus liable to be taken up is not constant, it is dangerous to rely on this method for medicinal or analytical purposes.

The detection of prussic acid is very simple. 1st. Its solution gives, with nitrate of silver, a white precipitate, cyanide of silver, insoluble in strong nitric acid when cold, but dissolved by boiling; it is insoluble in ammonia. If a liquor containing even a very small trace of prussic acid be boiled, the vapour produces a white cloud on a piece of glass moistened with solution of nitrate of silver. 2d. If a solution of sulphate of iron be added to prussic acid, there is no change; but on adding some potash liquor, a dirty greenish precipitate is produced, from which muriatic acid dissolves out the excess of oxide of iron, and leaves Prussian blue (cyanide of iron) of a very rich colour: it is essential to the proper action of this test, that both protoxide and peroxide of iron be present in the solution. 3d. If a solution of sulphate of copper be added to the liquor containing prussic acid, and then treated successively with potash and muriatic acid, as above, a white precipitate remains undissolved, which is cyanide of copper. The theory of these last actions is, that the prussic acid is too weak to decompose, by itself, either metallic sulphates, but, on the addition of potash, double decomposition occurs, sulphate of potash and a metallic cyanide being formed. As the potash is always added in excess, a quantity of metallic oxide is at the same time precipitated, which masks the colour of the result, but is removed by the addition of the muriatic acid. 4th. These insoluble cyanides may be recognised very elegantly by heating them with a little potash and sulphur, and dissolving the

fused mass in water. The solution gives, with a persalt of iron, a fine blood-red colour. 5th. The cyanide of silver, also, is known by giving off cyanogen when heated.

There are two *chlorides of Cyanogen* of the same composition, and bearing to each other the same relation as the cyanic and cyanuric acids. One is gaseous, the other solid; the first is prepared by acting on moist cyanide of mercury by chlorine, or by passing chlorine into weak prussic acid, and warming the mixture in which the chloride of cyanogen dissolves. This gas, which is very irritating and poisonous, may be obtained crystallized in needles by exposure to a very low temperature. It combines with ammonia, forming a crystalline substance.

The solid chloride may be prepared by acting on anhydrous prussic acid with chlorine, or by heating sulphocyanide of potassium in a current of chlorine. It sublimes in white transparent needles. It dissolves unaltered in alcohol and ether, and is decomposed by hot water into hydrochloric and cyanuric acids.

Iodide of Cyanogen is prepared by distilling, in a retort, a mixture of iodine, cyanide of mercury, and water. At a moderate heat, the iodide of cyanogen passes over, and condenses in the neck of the retort as a flocculent mass of snow-white needles. These crystals irritate the eyes: they dissolve in water unaltered, and volatilize at 113°.

SECTION II.

OF THE METALLIC CYANIDES.

Cyanide of Potassium, K.Cy., may be formed by the direct union of its elements, or by adding an excess of prussic acid to a solution of potash, and evaporating rapidly without the access of air. It is produced also whenever carbonaceous matter is calcined in contact with potash, provided nitrogen be present. The best mode of obtaining it, however, is to expose the yellow prussiate of potash to a full red heat, in a close iron crucible. The cyanide of iron is decomposed, nitrogen being given off, and carburet of iron remaining with the unaltered cyanide of potassium. The half-melted mass is to be coarsely powdered, and digested in boiling, weak spirit of wine, from which the salt crystallizes in cubes on cooling. Spirit of specific gravity 0·900 at 60°, is remarkable for dissolving a large quantity of cyanide of potassium when boiling, but depositing it nearly totally when it cools.

This salt in solution reacts alkaline, and smells of bitter almonds, and hence probably decomposes water when dissolved. Its crystals deliquesce and are decomposed, even in close vessels, after a short time, by contact with water, into ammonia and formiate of potash.

The properties of the cyanide of sodium and of the hydrocyanate of ammonia are quite similar.

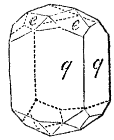
The *Cyanides of Barium*, strontium, calcium, and magnesium are soluble in water, and crystallizable.

Cyanide of Zinc is prepared by adding prussic acid to a solution of acetate of zinc, when it precipitates as a white powder. Chloride of zinc is not decomposed by prussic acid. With cyanide of potassium it forms a double salt.

Cyanide of Copper is formed as a whitish precipitate when prussic acid and potash are added to a solution of sulphate of copper. When boiled it becomes yellow, and combines with the oxide of copper to form an *oxycyanide* of a lively green colour. It forms double salts with the alkaline cyanides.

Cyanide of Mercury—Hg.Cy.; Eq. 1594·4 or 127·45—may be prepared by boiling two parts of Prussian blue with one of red oxide of mercury and eight of water, until the residue becomes red-brown. The filtered liquor yields cyanide of mercury in crystals, which, however, are not quite free from iron, and require to be digested with a little more oxide of mercury and recrystallized. The best

mode of preparing it is to distil fifteen parts of yellow prussiate of potash, with thirteen of oil of vitriol and 100 of water, nearly to dryness, and to digest the prussic acid so obtained with twelve parts of finely-powdered oxide of mercury, until this is completely dissolved. The solution yields, by evaporation and cooling, fourteen parts of pure crystallized cyanide of mercury. By washing out the residue in the retort with water, five parts of pure Prussian blue may be obtained.



Cyanide of mercury crystallizes in colourless rectangular prisms, as *q q*, in the figure, terminated by numerous secondary faces, as *e e*. These crystals are anhydrous, and occasionally opaque. When heated, it is resolved into mercury and cyanogen, of which a portion is resolved into the brown powder (paracyanogen). It is sparingly soluble in alcohol. It tastes as the other mercurial salts. So great is the affinity of mercury to cyanogen, that cyanide of potassium, when boiled with oxide of mercury, is decomposed, and caustic potash liberated. In a solution of cyanide of mercury, no test indicates the presence of the metal except sulphuretted hydrogen. It is not decomposed by oxygen acids, but muriatic acid forms prussic acid and chloride of mercury.

Cyanide of mercury, when digested with an excess of oxide of mercury, combines with it in two proportions, forming the *oxycyanides of Mercury*, Hg.Cy.+Hg.O. and Hg.Cy.+3Hg.O. These bodies are soluble in water, and crystallize in prismatic needles.

With iodide of potassium, cyanide of mercury combines, forming a substance, 2 Hg.Cy.+K.I., which is very soluble in boiling water, and crystallizes in brilliant white micaceous plates on cooling. This salt is instantly reddened by any mineral acid which liberates iodide of mercury. With sulphocyanide of potassium a similar compound is formed, 2Hg.Cy.+K.Cy.S_2.

Cyanide of mercury combines with the alkaline cyanides, and with the alkaline chlorides and bromides, forming double salts possessing no special interest. It combines with many oxygen salts also, as the chromate and formiate of potash.

As prussic acid is now no longer prepared from cyanide of mercury, this body is not so important as formerly. It is poisonous, and is occasionally employed in medicine.

Cyanide of Silver, Ag.Cy., is a white powder insoluble in water, which combines with other cyanides to form double salts. It is soluble in water of ammonia, but insoluble in nitric acid, except it be strong and boiling. Heated, it gives cyanogen and metallic silver.

Cyanide of Palladium.—In its affinity for cyanogen, palladium resembles mercury. Every soluble salt of palladium is decomposed by prussic acid, a pale yellow precipitate being formed. This cyanide of palladium is insoluble in water, but soluble in acids and in ammonia. Heated, it gives cyanogen and leaves the metal. It forms a very extensive class of double salts.

Cyanide of Gold, Au.Cy_3, is a pale yellow powder, forming double salts with the alkaline cyanides.

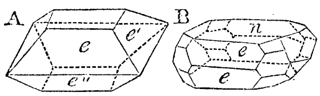
Protocyanide of Iron, Fe.Cy., is not known in an isolated form, but it enters into combination with the other metallic cyanides, forming double salts, which are some of the most interesting of the cyanogen compounds. The iron in these salts cannot be separated by an alkali, and hence may be looked upon as an element of the negative constituent; they are hence often termed *ferrocyanides*, or *ferroprussiates* of whatever other metal they may contain.

Ferrocyanide of Hydrogen. Ferrocyanic Acid.—Fe.Cy.+2H.Cy When the ferrocyanide of lead is decomposed by sulphuret of hydrogen, a solution is obtained, which yields, on evaporation in vacuo, small granular crystals, which have a well-marked acid reaction, and produce, by acting on metallic oxides, all the ordinary ferrocyanides. If the solution be boiled, it is resolved into prussic acid,

and a white precipitate, which becomes blue in the air. The crystals undergo the same change spontaneously after some time.

Ferrocyanide of Potassium.—Fe.Cy.+2K.Cy.+3 Aq. Eq. 2656·9 or 212·5. This compound, of which I have often spoken as *Yellow Prussiate of Potash*, is prepared on the large scale for the purposes of the arts and of pharmacy, by calcining together some animal matters, as blood, hoofs, horns, &c., with pearl ashes and iron filings. It may be formed even if the organic matter do not contain nitrogen, as that element may be supplied from the air. The operation is conducted in large iron pots arranged in a furnace, so that the mass can be heated to dull redness, and continually agitated as it forms a tenacious paste, the calcining of which is continued as long as it burns with a white flame; it is then taken out of the pot, and when cold, boiled in water, which, by evaporation, yields the salt in crystals. If it has not dissolved iron enough, some copperas is added as long as the Prussian blue, which at first forms, is found to redissolve. After what has been said of the formation of cyanogen (p. 513), the theory of this process may easily be understood.

The ferrocyanide of potassium crystallizes in truncated octohedrons with a rectangular base, *e e′ e″*, as in the figure, of which A represents the usual simple, and B a more complicated form; the secondary plane *n* often being so large as to render the crystal merely tabular. Its colour is fine citron-yellow, but when dried it becomes white. By a farther heat in close vessels it fuses, and when ignited gives off nitrogen, and leaves cyanide of potassium and carburet of iron. Heated in open vessels, it absorbs oxygen, and forms cyanate of potash. Its use in the preparation of these bodies and of prussic acid has been already detailed. If it be digested with oxide of mercury, cyanide of mercury is formed, and oxide of iron and caustic potash set free. With sulphate of mercury it gives sulphate of potash, cyanide of mercury, and Everitt's yellow salt.



With cyanide of mercury, ferrocyanide of potassium forms a double salt, whose formula I found to be 3Hg.Cy.+(Fe.Cy.+2K Cy.)+4 Aq. It crystallizes in pale yellow rhombic tables.

In the arts, the ferrocyanide of potassium is of importance for dyeing various shades of blue; to the chemist it is specially of interest, as from it all the cyanogen compounds are most economically formed, and from the peculiar precipitates it gives with solutions of most metals, it is of eminent service in their detection. Thus, with solutions of *silver*, *mercury*, *bismuth*, *tin*, *lead*, *nickel*, *zinc*, *manganese*, and *cerium*, it gives white precipitates; that with mercury gradually becomes blueish, and that of manganese reddish. With *copper*, the precipitate is of a rich chocolate colour; with *cobalt*, greenish, changing to red; with *uranium* and *molybdenum*, brown; and with *chrome*, grayish-green. All these precipitates contain cyanide of iron, united to two atoms of cyanide of the other metal, being true *ferrocyanides*.

It is on solutions of *iron* that the action of this reagent is the most remarkable. With solution of protosulphate of iron, a whitish precipitate is obtained, which consists of the cyanides of iron and po-

tassium, united in proportions which are not well known. Exposed to the air, this body absorbs oxygen and becomes blue. With a solution of sulphate of iron pure *Prussian Blue* is precipitated. This substance is insoluble in water and in muriatic acid, and gives with caustic alkalies oxide of iron and ferrocyanide of potassium; its formula is Fe_7Cy_9, or it consists of $3Fe.Cy.+2Fe_2Cy_3$. Its formation involves $3(Fe.Cy.+2K.Cy.)$ and $2(Fe_2O_3+3S.O_3)$, and there remain dissolved six atoms of sulphate of potash. For the manufacture of Prussian blue for the purposes of the arts, the impure liquor obtained by digesting in water the calcined mass of animal matter, potash and iron, described p. 522, is decomposed by an excess of sulphate of iron, and the resulting precipitate digested in muriatic acid, and exposed to the air until it assumes its proper colour. It is then dried carefully at a moderate heat.

Another kind of Prussian blue is produced when Everitt's salt, or the white precipitate produced by protosulphate of iron with yellow prussiate of potash, is exposed moist to the air. It is termed *basic Prussian Blue.* As Everitt's salt consists of $2Fe.Cy.+K.Cy.$, and this last dissolves out, there is the same number of atoms of cyanogen and iron, and the excess of iron above that necessary to form true Prussian blue combines with the oxygen of the air, the oxide so formed remaining united with the Prussian blue. From 9 Fe.Cy. and 3O. there is thus formed $3(Fe.Cy.+2Fe_2Cy_3+Fe_2O_3)$, the basic compound.

The *ferrocyanides of Sodium, Barium,* &c., possess all the essential characters of the potassium salt, and need not be farther noticed.

The ferrocyanides in many cases combine with each other, forming salts, which contain three different metals combined with cyanogen.

Sesquicyanide of Iron, Fe_2Cy^3, is not known in an isolated form, but, like the protocyanide, enters into a number of combinations with the other metallic cyanides, which may be called either *perferrocyanides* or *ferridcyanides*, as proposed by Liebig.

Ferridcyanide of Potassium—Red Prussiate of Potash, $Fe_2Cy_3+3K.Cy.$, is formed by passing chlorine through a solution of yellow prussiate of potash until it ceases to give Prussian blue with solution of persulphate of iron. The liquor becomes of a deep green colour, but on evaporation yields anhydrous fine ruby-red prismatic crystals, which are generally macles. The products of its decomposition by heat are the same as those of the yellow salt. It dissolves in thirty-eight parts of cold water; its solution, if pure, is yellow, but more commonly is green.

This salt rivals that already described in its utility as a reagent for the proper metals. The precipitates it gives with their solutions are, *tin*, white; *mercury*, *silver*, and *zinc*, yellow; *titanium*, *nickel*, *copper*, and *bismuth*, yellowish brown; and *cobalt*, *uranium*, and *manganese*, brown. It is, however, with the salts of *iron* that its reaction is most remarkable. With a persalt of iron it merely colours the liquor green, but with a solution of a protosalt it gives a blue precipitate, even richer in colour than the proper Prussian blue, and consisting of Fe_5Cy_6, or of $Fe_2Cy_3+3Fe.Cy.$; thus containing the same protocyanide with half as much sesquicyanide as exists in common Prussian blue. This *ferridcyanide of Iron* is made for commerce, and sold as *Turnbull's Prussian Blue.*

Ferridcyanide of Hydrogen.—If we digest ferridcyanide of lead

with dilute sulphuric acid, a red liquor is obtained, which yields on evaporation a mass of minute brownish-yellow needles, the formula of which is $Fe_2Cy_3+3Cy.H$. This body reddens litmus, and has a sour astringent taste; upon another theory it is considered to be a compound of hydrogen with a compound radical, (Fe_2Cy_6), and is termed *Ferridcyanic Acid.*

In the history of these complex cyanides we meet three facts, on which the theories of their constitution must be founded. 1st. The extraordinary tendency to double combination, which no other body possesses in the same degree. 2d. In almost all cases, the cyanogen enters into the compound in the proportion of three, six, or nine atoms; and, 3d. One metallic element, as iron, in each compound, is retained with extraordinary force, not being detected therein by its ordinary reagents. The original view proposed by Berzelius, of considering these compounds as mere double salts, and upon which the formulæ given hitherto have been constructed, does not account sufficiently for these facts, and I hence consider it as less applicable to them than the theories suggested by Graham and by Liebig.

The latter chemist founds his view upon the third fact, and supposes that there exists a series of compound radicals, consisting of cyanogen united with a metal. Thus, *Ferrocyanogen*, ($Fe.Cy_3$) or Cfy., and *Ferridcyanogen*, (Fe_2Cy_6) or Cfy_2, these two being isomeric; *Cobaltocyanogen*, (Co_2Cy_6) or Cky., and many others; and these radicals combine with hydrogen to form polybasic hydracids, from which, the hydrogen being replaced by a metal, result the ordinary complex cyanides. Thus, the ferrocyanogen being bibasic, its acid is Cfy.+2H.; its potash salt, Cfy.+2K.; its copper salt, Cfy.+2Cu.; and if each atom of hydrogen be replaced by a different metal, then the triple salts formed by Mosander are produced: thus, the salt written on Berzelius's view as (Fe.Cy.+2K.Cy.)+(Fe.Cy.+2Ca.Cy.) becomes Cfy.+Ca.K., and similarly there is Cfy.+Ca.K., &c.

The red prussiate of potash Liebig supposes to contain a radical, (Fe_2Cy_6) or Cfy_2, isomeric with, but of double the atomic weight of ferrocyanogen; this *ferridcyanogen* forms with hydrogen a tribasic acid, Cfy_2+H_3, by replacement of the hydrogen, in which, by three atoms of the same or of different metals, the various *ferridcyanides* are produced, as Cfy_2+K_3, $Cfy_2+3Cu.$, &c.

The Prussian blues, on this theory, are considered to be compounds of ferrocyanide with ferridcyanide of iron; thus,

$3Cfy.Fe_2+Cfy_2Fe_3$ expresses common Prussian blue.
Cfy_2Fe_3 " Turnbull's Prussian blue.
$3Cfy.Fe_2+Cfy_2Fe_3+Fe_2O_3$ " basic Prussian blue.

This theory accounts very strictly for the first and third of the fundamental facts which I have described as characterizing the cyanogen compounds. The theory of Graham is specially based upon the tendency of three atoms of cyanogen to enter together into combination with other bodies, as is shown not only in its relation to metals, but to oxygen, as in cyanuric acid, and hence we may assume that cyanogen, as Cy_3, with three times its ordinary atomic weight, forms a distinct radical (*paracyan?*), which forms with oxygen and with hydrogen tribasic acids, Cy_3O_3 and Cy_3H_3. From the replacement of more or less of this hydrogen in the latter by equivalents of one or more metal, the various cyanides may be formed. Thus, for example,

$Cy_3+Fe.2K.$ . . . yellow prussiate of potash.
$Cy_3+Fe.K.Ca.$ . . ferroprussiate of lime and potash.
$Cy_3+Fe.2H.$ . . . ferroprussic acid.

The basis of the red prussiate of potash should be, then, another polymeric cyanogen, Cy_6, which would form, with hydrogen, a pentabasic acid, Cy_6+H_5, in which more or less of replacement by metals should give the various ferridcyanides. Thus ferridprussic acid should be $Cy_6+Fe_2H_3$, and red prussiate of potash $Cy_6+Fe_2K_3$, and so on; Turnbull's Prussian blue becomes, on this theory, simply Cy_6+Fe_5; the common Prussian blue is $(Cy_3+Fe_2)+Cy_6Fe_5$; and, by the addition of Fe_2O_3 to that, the basic Prussian blue is formed.

I am rather inclined to adopt Graham's view, although, in the present state of our knowledge, we have not grounds for positive decision. He proposes to term the radical Cy_3 *Prussine*, but has not given any name to that whose formula is Cy_6.

Of Sulphocyanogen, and the Products of its Decomposition.

If yellow prussiate of potash, well dried, and mixed carefully with half its weight of sulphur, in fine powder, be heated in an iron vessel to perfect fusion, which takes place at a dull red heat, the sulphur combines with all the cyanogen, forming sulphocyanogen, which unites with the potassium, while the iron is converted into sulphuret. By digesting the fused mass in water, the former dissolves, and is obtained, by evaporation and cooling, in long striated prisms, similar to those of nitre. If the temperature be not raised too high, the iron forms also sulphocyanide, which dissolves, and may be decomposed by the addition of a slight excess of carbonate of potash; by this means one half more product may be obtained than is yielded if the sulphocyanide of iron be too violently heated, and thereby converted into sulphuret.

Sulphocyanogen is prepared by passing a current of chlorine gas into a solution of the salt thus formed, or by heating it in dilute nitric acid; chloride, or nitrate of potassium is formed, and a deep yellow precipitate produced, which contains all the sulphur and cyanogen of the salt, its formula being $Cy.S_2$. It is very light, and insoluble in water. It combines with all the metals and with hydrogen, forming well-defined salts.

Hydrosulphocyanic Acid, $Cy.S_2+H.$, is formed by decomposing sulphocyanide of lead by dilute sulphuric acid, or by sulphuret of hydrogen. It is a colourless liquid, which reacts, and tastes acid. By distillation it is decomposed.

Sulphocyanide of Potassium.—$Cy.S_2+K.$ This salt, of which the mode of preparation has been just described, forms anhydrous prisms, cool and pungent in taste; it is abundantly soluble in water and alcohol, and slightly deliquescent. It is employed in the laboratory as a test for peroxide of iron.

Sulphocyanide of Lead is a crystalline powder, prepared by mixing solutions of a salt of lead and of sulphocyanide of potassium.

Of the *sulphocyanides of Iron*, the protosalt, $Fe.+Cy.S_2$, forms a colourless solution, which becomes red on exposure to the air. The sesquisalt, $Fe_2+3Cy.S_2$, forms a deep blood-red liquor, when a soluble sulphocyanide is mixed with any salt of the peroxide of iron. It serves thus as a very delicate test of the presence of iron, and also for that of cyanogen; it is so applied to the detection of prussic acid, as noticed p. 520.

These sulphocyanides may be considered either as double sulphurets of cyanogen and of a metal, as $Cy.S.+S.K.$, &c., or as salts of the compound radical sulphocyanogen, $Cy.S_2+K.$, &c. The latter view has been almost universally adopted by chemists.

It appears, however, from the researches of Parnell, that although sulphocyanogen really exists in these salts, yet the yellow substance extracted from them by chlorine or by nitric acid, as described just now under that name, is only a product of the decomposition of the real sulphocyanogen, which has not been as yet isolated. The formula of the yellow powder he finds to be $S_{12}C_{12}N_6 . H_3O$. When acted on by alkalies or by nitric acid, it produces an acid which he terms the *Thiocyanic*, which is polybasic. It is a

pale yellow powder, sparingly soluble in water, more so in alcohol. Its formula is $S_{12}C_{10}N_5 . H_6O_2$. Its compounds with the oxides of lead, silver, mercury, &c., are insoluble. This new acid is but one of the bodies produced in this reaction; the others have not been examined.

Mellon.—When sulphocyanogen is heated, it is decomposed, yielding sulphur, sulphuret of carbon, and a yellow powder which remains as fixed residue, and to which Liebig has given the name of *Mellon.* This is a compound radical, analogous to cyanogen in its characters. It is insoluble in water, alcohol, or dilute acids. Its formula is C_6N_4 or Ml., and when strongly ignited it is decomposed into three volumes of cyanogen and one of nitrogen. Heated with potassium, they unite with combustion; and if it be fused with the iodide or bromide of potassium, iodine or bromine is expelled, and mellonide of potassium formed.

Hydromellonic Acid, H Ml., is formed by dissolving mellonide of potassium in boiling water, and adding a strong acid. A gelatinous white precipitate forms, which dries into a yellowish powder, H.Ml.+Aq.

Mellonide of Potassium, K.Ml., is produced by adding mellon to sulphocyanide of potassium, fused in a porcelain capsule; sulphur and sulphuret of carbon are evolved. On dissolving the brown mass thus formed in boiling water, the mellonide of potassium crystallizes, on cooling, in fine colourless needles.

If we take the formula of sulphocyanogen at $C_2N.S_2$, the formation of mellon consists in $4(C_2N.S_2)$, producing $2(C.S_2)$ with 4S., and leaving C_6N_4; but, on Mr. Parnell's view, the decomposition is by no means so simple.

When mellon is boiled with strong nitric acid, it dissolves, and, on cooling, the liquor yields octohedral crystals of *Cyanilic Acid.* This substance has the same formula as cyanuric acid, Cy_3O_3+3 Aq., but its relations to bases are not well understood. Nitrate of ammonia is formed; mellon, C_6N_4, and three atoms of water, giving $C_6N_3O_3$ and $N.H_3$.

Melam.—$C_{12}H_9N_{11}$. Sulphocyanide of ammonium, on being heated, is decomposed into ammonia, sulphuret of carbon, and sulphuret of hydrogen, which pass off, while a grayish-white powder remains, which is *Melam.* The same result is obtained by heating to fusion a mixture of sulphocyanide of potassium and sal ammoniac: in this case chloride of potassium also remains behind, but may be removed by washing. Melam is insoluble in water and alcohol. It is dissolved and decomposed by boiling acids and alkaline solutions, giving origin to a series of remarkable bodies.

Melamine. $C_6C_6N_6$, is prepared by boiling melam with a dilute solution of caustic potash until the liquor becomes quite clear; it is then to be evaporated until it begins to deposite small crystalline plates, and being then allowed to cool, the mellamine crystallizes out in colourless octohedrons, scarcely soluble in cold water. It has no action on vegetable colours, but it combines with dilute acids, acting as a base, and forming well-defined salts, which have an acid reaction, and may be obtained crystallized.

Ammeline.—$C_6N_5 . H_5O_2$. After the alkaline solution has deposited the melamine by cooling, it contains ammeline, which precipitates when acetic acid is added. This is to be purified by solution in dilute nitric acid, and precipitation by carbonate of ammonia. It then forms fine silky needles, insoluble in water and alcohol. It combines with the dilute acids, forming crystallizable salts.

The origin of these bodies consists in the melam decomposing two atoms of water, and then $C_{12}H_{11} . N_{11}O_2$ producing $C_6H_6N_6$ and $C_6N_5 . H_5O_2$. By boiling melam in dilute muriatic acid, the same decomposition occurs, and the muriates of melamine and ammeline crystallize together on cooling.

If any of the above three bodies be dissolved in strong sulphuric acid, and the solution be precipitated by alcohol, a white powder is obtained, insoluble in water and alcohol, but soluble in strong acids and alkalies. It is nearly indifferently acid or base, as it combines with nitric acid, and also with oxide of silver. It is termed *Ammelide.* Its formula is $C_{12}H_7 . N_9O_4+2$ Aq. When this body is boiled for a long time with dilute sulphuric or nitric acid, it is resolved into ammonia and *Cyanuric Acid,* which last is the ultimate product of the similar treatment of all the bodies of this series.

The theoretical constitution of these bodies remains exceedingly obscure. The bases, melamine and ammeline, are of great importance, from their close analogy to the alkaloids, which are found naturally in many plants; but still we have no idea of the mode of arrangement of their elements.

Some other sulphur compounds of cyanogen are known, but do not require much notice. Cyanogen and sulphuretted hydrogen combining, form orange crystals, insoluble in water.

CHAPTER XX.

OF STARCH, LIGNINE, GUM, AND SUGAR, WITH THE PRODUCTS OF THEIR DECOMPOSITION BY ACIDS AND ALKALIES.

The substances now to be described form a very remarkable class of organic bodies. They are found abundantly in most plants, but varying somewhat in characters, according to their immediate source, and are subservient to the most important offices of the vegetable organization, being the materials from whence the tissues and secretions of the plant are elaborated. In a chemical point of view, they are distinguished by a remarkable similarity of composition, all containing the same quantity of carbon (twelve atoms) in the equivalent, united to oxygen and hydrogen, which are always present in the proportions to form water. In this may be found the cause of the extraordinary transmutations of these bodies from one to another, by the mere fixation of the elements of water, effected by the influence of reagents, or by the organic power of the plant. In these bodies, also, we find an example of the difficulty of distinguishing between a constitution derived from physical, and that resulting from vital force. In the different kinds of sugar, the crystalline condition, solubility, &c., indicate that the elements are combined by forces merely chemical; but in the different varieties of starch, and especially in lignine, traces of organized structure are found, and properties manifested, which attach their history as closely to the physiology as to the chemistry of plants. Under this point of view they shall be hereafter reconsidered.

Of Starch, its Varieties and Products.

The most important variety of this principle is that known as *Common Starch.* It exists in most plants, and in all parts of them. It is extracted from the seeds of wheat and barley; from the tubers of the potato; from the root of the jatropha manihot, as *Tapioca* or *Cassava*, and of the maranta arundinacea, as *Arrow-root;* and from the stems of palms, as the sagus rumphii, which furnishes the *Sago* of commerce. The starch is imbedded in the cellular tissue of the plant as small white grains, totally destitute of any crystalline structure. They differ in size in almost every plant. Those of the potato, which are the largest, do not exceed in diameter $\frac{1}{250}$th of an inch; those of arrow-root, which are some of the smallest, do not exceed $\frac{1}{600}$th. In form, these grains vary also, some being globular,

others ovoidal, and often, even in the same plant, irregular. Each grain is formed by a number of concentric layers, which increase in density and consistence from the centre; the most external being so hard as to resemble a membranous envelope filled by a softer material.

The grains of starch are quite insoluble in cold water; in boiling water they dissolve, except the outer layers, which, floating in the liquor, give it a peculiar opalescent aspect. On cooling, the solution gelatinizes. If the solution of starch be dried at a gentle heat, and then digested with cold water, the outer layers of the grains may be separated by filtration, and a colourless transparent solution of starch thus obtained.

The preparation of starch rests on its insolubility in cold water. The texture of the plant is first broken up by rasping or coarse grinding, and being then mashed up with water, the starch grains fall out from the ruptured cells, and are carried off by the current, from which they deposite themselves when the liquors are left at rest. In obtaining starch from wheat, this liquor is allowed to ferment and become sour, by which a quantity of gluten that would otherwise attach itself to the starch is removed. If the moist starch grains be dried at a temperature of about 140°, they gelatinize to a semitransparent mass, which remains so when dried, and is not granular or mealy. It is thus that the peculiar aspect of tapioca and sago is produced.

By the vital action of the seed in germination, the transformation of starch into sugar is effected, and constitutes the *saccharine fermentation*. It is artificially induced by *malting* the grain, for the preparation of alcoholic liquors by brewers and distillers. The circumstances of this change will be specially noticed when describing the mode of nutrition and of the growth of plants.

If starch be heated beyond 240°, it softens and becomes brown. If the heat be increased until the mass smokes, it is found to be changed into a substance totally soluble in cold water, and known as *British Gum.*

The action of reagents on starch is very remarkable. By boiling with dilute sulphuric or muriatic acids, a kind of saccharine fermentation is induced, it being changed successively into gum, sugar, and sacchulmine. By boiling with nitric acid, it gives saccharic and oxalic acids. These reactions will be hereafter studied in detail. A solution of it is precipitated by basic acetate of lead and by infusion of galls. With bromine it gives a yellow precipitate, which is decomposed by heat, the bromine being expelled. With iodine it produces a compound of an intense blue colour, which is its most remarkable property.

Iodide of Starch is produced when a solution of free iodine is added to a solution of starch. Its colour is violet blue or nearly black, according to the proportion of starch. It is very soluble in water, but insoluble in alcohol, and may be obtained solid by adding alcohol to a very strong aqueous solution, and collecting the precipitate on a filter. It is decomposed by alkalies and by chlorine; indeed, by all bodies which combine with iodine; and its formation serves, therefore, as a test only for free iodine, as described in p.

313. When a solution of iodide of starch is heated, it becomes quite colourless below 200°, and, if it be not boiled, regains its colour perfectly as it cools. When the liquor remains colourless after cooling, the blue may be restored by oxalic acid or by chlorine, which expels the iodine from the combination it had formed.

The composition of starch, no matter what plant it may be derived from, is $C_{12}H_{10}O_{10}$, as confirmed by a variety of reactions. Its combination with oxide of lead, *Amylate of Lead*, is $C_{12}H_{10}O_{10}+2 Pb.O$.

Inulin.—This kind of starch is found in the roots of the inula, dahlia, angelica, leontodon, and many other plants. It may be prepared in the same way as common starch. It is a white and very fine powder, almost insoluble in cold water, but easily dissolved by boiling water; forming a liquor which becomes thick, but not gelatinous, when it cools, and deposites the greater part of the inulin unchanged. It is transformed by acids, like common starch, but more easily. It is precipitated, like it, by solutions of borax and subacetate of lead, and by infusion of galls. It is peculiarly distinguished from it by not giving with iodine any blue colour, being merely tinged yellow. The structure of the grains of inulin has not been accurately examined. Its formula is $C_{12}H_{10}O_{10}$, like that of common starch, but in combining with oxide of lead it appears to lose one atom of water, and to become $C_{12}H_9O_9$, as remarked by Parnell.

Lichenine.—This variety of starch, which is found in many lichens, especially the Iceland moss and the carrigeen (sphœrococcus crispus), is not contained in the plant in grains, but in a soluble condition. To obtain it, the lichen is first digested in a cold dilute solution of carbonate of soda, to dissolve the bitter resinous principle, and this being completely washed away, the lichen is boiled for a long time in water; a liquor is obtained, from which, on cooling, the lichenine separates as an opaque gray jelly, which, when dried, is black, hard, and glassy. Its properties are very similar to those of inuline. It gives with iodine a greenish-brown colour. Its composition is expressed by the same formula as the others, $C_{12}H_{10}O_{10}$.

Of Lignine. Principle of Woody Fibre.

When any kind of wood is treated successively and repeatedly by dilute acids and alkalies, by water and by alcohol, so that every soluble material is removed from it, we find that the substance which remains is of very constant composition, being expressed by the formula $C_{12}H_8O_8$. Of this substance, *Lignine*, the proper wood of the plant is constituted; its molecules being arranged so as to form the tubes and cells of the vegetable tissues, and cohering so firmly as to produce the fibres of flax, cotton, and hemp, which constitute the materials of our most important woven textures, of paper, &c. Although the lignine is thus rather the remains of an organized body than a mere chemical substance, it forms some combinations which are of great importance in the arts. Thus, if linen or cotton cloth be dipped in dilute solution of acetate of alumina, the earth abandons the acid to combine with the lignine, and thus serves as the means of fixing on the cloth the various colouring matters used in the processes of dyeing. The same occurs with oxide of iron; and other metallic oxides have a similar, though weaker affinity for lignine, and thus serve as *mordants* for various colours.

Lignine, when quite pure, is white; the bleaching of linen, cotton, paper, &c., being effected by destroying, by means of the air or of chlorine, the resinous and other matters which are associated with the lignine in the fibres or cells of the plants; the lignine itself resists these agents, unless applied in a very concentrated form

With cold nitric acid lignine combines directly, forming a very remarkable substance, *Xyloïdine*, which may be produced by immersing for a moment a piece of paper in strong nitric acid, and then washing it well in pure water. It assumes the feel and toughness of parchment, and is so combustible as to serve for tinder. Hot nitric acid converts lignine into oxalic acid; with sulphuric acid it is changed into gum, and ultimately into sugar, as will be detailed farther on.

If sawdust be heated with a warm solution of potash for some hours, the liquor will be found to contain a considerable quantity of common starch, capable of striking a blue colour with iodine; but by this means the ligneous fibre is dissected, and not decomposed. The starch may be extracted also by mechanical means, and pure lignine does not yield any. If lignine be strongly heated with hydrate of potash, hydrogen is evolved, and a mixture of acetate and oxalate of potash results; $C_{12}H_8O_8$ and 4H.O. giving 6H., with $2(C_2O_3)$ and $2(C_4H_3O_3)$.

In dry air, or immersed under water free from air, lignine remains for an indefinite length of time unaltered; but if both air and water have access, oxygen is absorbed, and carbonic acid and water given out, and a series of products of decomposition result, which form the basis of *vegetable soil*, and thus serve as the materials for a new generation of plants. By the conjoint action of heat and water, lignine produces another class of products, and a third series arises from the destructive distillation of dry wood. These subjects will be examined specially in their proper place.

Of the different Varieties of Gum.

It is necessary to distinguish three varieties of gum, to which the names of *Arabine*, *Cerasine*, and *Dextrine* may be given. The first two are natural, the last is a product of the transmutation of starch.

Arabine is found in the juices of many species of acacia and prunus; it exudes from crevices in the bark, and forms lumps, in which state it is found in commerce (*Gum Arabic* and *Gum Senegal*). The roots of mallow, comfrey, and many other plants contain a great deal of arabine. It is never crystalline, and is colourless and transparent, with a vitreous fracture. It is dissolved by water in all proportions, forming a thick, adhesive liquid (*mucilage*). It is not dissolved by alcohol, which precipitates its watery solution. It combines with bases, forming well-defined, insoluble compounds, and is not in any way acted on by iodine. A solution of arabine exercises sinistral rotatory power on a ray of polarized light (p. 41). By contact with sulphuric acid, arabine is gradually converted into dextrine, and, if the digestion be continued, this then changes into sugar. With nitric acid arabine gives mucic acid, and afterward oxalic acid; another characteristic property of it is, that of giving a precipitate with solution of silicate of potash (soluble glass, p. 437). Its composition is expressed by the formula $C_{12}H_{11}O_{11}$.

Tragacanthine, or *Vegetable Mucus*, exists in cherry-tree gum mixed with arabine, but is purer in gum tragacanth, in flaxseed, and in quince-seed. It is extracted by digestion in water, when it gradu-

ally swells up and appears rather to imbibe the water than to dissolve; a thick tenacious liquor is obtained, which is precipitated by alcohol and by solution of basic acetate of lead, but not by silicate of potash. With sulphuric and nitric acid, the same products are formed as from arabine.

The *Salep* of commerce is the tragacanthine extracted from the roots of various species of orchis, and dried.

Dextrine.—This variety of gum is formed from the starch of the seed, in germination, and may be obtained by digesting starch in dilute sulphuric acid. If five parts of starch, with one of oil of vitriol and fifteen of water, be kept at 200° for some time, the starch completely disappears, the solution loses its power of gelatinizing; it acquires the characteristic rotatory power of *Dextrine*, and colours iodine of a port-wine red, without any tinge of blue. If the liquor be neutralized by carbonate of barytes, the whole quantity of sulphuric acid separates, and by evaporation, the dextrine is obtained as a pale yellow mass of a vitreous fracture; it is not adhesive like common gum, nor does it yield any mucic acid when acted on by nitric acid.

Dextrine precipitates a solution of basic acetate of lead, but is not affected by silicate of potash. If dextrine be boiled too long with the sulphuric acid, it passes into a substance more analogous to tragacanthine, which is also formed when arabine or lignine is so treated. In this state its rotatory power is feeble, and it is not at all coloured by iodine. In both these forms the composition of dextrine is $C_{12}H_{10}O_{10}$.

Of the different Varieties of Sugar.

The species of sugar are much better distinguished from each other, both by properties and composition, than the various kinds of starch, or of gum, have been found to be. They are all characterized by being capable of undergoing the alcoholic fermentation.

Cane-sugar.—$C_{12}H_{10}O_{10}$+Aq. when crystallized. This species of sugar is found abundantly in the juices of many plants. It is extracted for use from the sugar-cane, the maple, and the beet-root. The juice, when fresh, runs into fermentation with great quickness, and is therefore clarified by being warmed to 150°, with a little lime, by which the vegetable albumen is coagulated, and the fermentation checked. The juice is then evaporated with as little heat as possible, and allowed to cool in vessels, at the bottom of which a number of small apertures, stopped with plugs, are situated. The sirup congeals into a granular mass, and when it is quite cold, the apertures below are opened, and the liquid portion allowed to run out. The sugar thus obtained in fine crystalline grains is brownish-coloured, and is termed *Muscovado*, or *Raw Sugar*. The liquid uncrystallizable portion constitutes *Molasses*, or *Treacle*. To obtain the sugar pure, it is redissolved, and the liquor having been cautiously evaporated (in some establishments, *in vacuo*, see p. 85) to the necessary degree, is poured into cones of unglazed earthenware, which are placed on their summits, the orifice in which is stopped by a plug. When, by cooling, the sirup has crystallized, during which the mass is continually stirred about to render the

crystals very minute and close, the plug below is removed, and the coloured liquor drains out; the last portions of it being removed by laying a sponge, moistened with some spirit or with a clear sirup, on the sugar at the base of the cone, and allowing the pure liquid to filter through. Thus is obtained *refined*, or *Loaf-sugar*. If a strong sirup be laid aside in a warm place, it crystallizes in very beautiful oblique rhombs, which constitute the *Sugar-candy* of commerce.

Cane-sugar is perfectly colourless. Its sp. gr. is 1·6; when heated, it fuses at 350° into a clear yellow liquid, and congeals, on cooling, into a hard brittle mass (barley-sugar), which, after some weeks, becomes opaque, white, and crystalline. If the temperature rises to 630°, water is given off, and the sugar becomes dark brown, being changed into *Caramel;* more strongly heated, it is totally decomposed. Sugar dissolves in one third of its weight of cold, and in all proportions in boiling water. A saturated solution becomes quite solid when it cools. If a strong solution of sugar be kept for some time near its boiling point, it is gradually changed into uncrystallizable sugar; hence arises the most important source of loss in the manufacture and refining of sugar. It is sparingly soluble in absolute alcohol, and but moderately in weak spirit.

Sugar combines with some bases and salts, acting as a feeble acid; the compound with oxide of lead is insoluble, and has the formula $C_{12}H_{10}O_{10}+2Pb.O.$; that with barytes is crystalline: its formula is $C_{12}H_{10}O_{10}+Ba.O.$ With common salt sugar combines, forming crystals, easily soluble in water, and consisting of $C_{12}H_{10}O_{10}+Na.Cl.$

The action of acids on cane-sugar is very remarkable. When digested with very dilute sulphuric or muriatic acid, it is converted into grape-sugar; but with stronger acids, it is changed into two brown substances, insoluble in water, one of them soluble, the other insoluble in alkaline liquors. The former is termed *Sacchulmine*, the latter, *Sacchulmic Acid.* These bodies are formed even with very dilute acids if the digestion be continued for a long time. According as the reaction proceeds, the sacchulmine separates in minute brilliant brown crystalline plates, mixed with a dull brown powder, which is sacchulmic acid. They are separated by water of ammonia, which dissolves the latter. The composition of these bodies is not quite definitely established, as it appears to be influenced by the strength of the acid used and other circumstances. The best-grounded idea is, that they have both the same composition, $C_{30}H_{15}O_{15}$, being isomeric with ulmine. If in this reaction the atmospheric air have access, oxygen is absorbed, and a large quantity of formic acid generated.

The preparation of oxalic acid by means of nitric acid and sugar has been already described (p. 493). If dilute acid be used, so that the oxidation may not be forced so far, a liquor is obtained which gives with carbonate of lime a neutral solution. When this is de composed by acetate of lead, a white precipitate is thrown down, which being acted on by sulphuretted hydrogen, the acid is set free, and may be obtained crystallized by evaporating and cooling its solution. This is termed the *Saccharic Acid.* It gives an extensive series of salts, being a pentabasic acid. Its formula is $C_{12}H_5O_{11}+5$ H.O. when crystallized. Its potash salt is $C_{12}H_5O_{11}+K.O.\ .\ 4H.O.$

Its lead salt $C_{12}H_5O_{11}+5Pb.O$. The saccharate of lime is sparingly soluble in water, but dissolves in a very slight excess of acid, which distinguishes it from an oxalate. An ammoniacal solution of saccharate of silver is decomposed by heat; metallic silver being deposited, and forming a mirror-surface on the interior of the vessel.

The *Caramel* formed by heating sugar to 650° appears as a porous, shining, jet black mass. It is completely soluble in water, and free from any empyreumatic taste. It is insoluble in alcohol; it combines with bases; its formula is $C_{12}H_9O_9$. The sugar, in forming it, therefore, loses the elements of an atom of water, besides its water of crystallization. By heating sugar with lime, a volatile liquid is obtained, which has the formula C_6H_5O., and is termed *Metacetone*.

Grape-sugar. Glucose.—$C_{12}H_{11}O_{11}+3$ Aq. when crystallized. This kind of sugar is still more extensively distributed in nature than the former. It gives the sweet taste to fruits, and forms the solid part of honey. It is produced in the animal body in certain forms of disease, as diabetes, and by the transformation of starch in germination, and by artificial processes. In consequence of this variety of sources, it is better to term it glucose, as suggested by Dumas, than to use a name indicating any one special origin.

Glucose may be obtained from raisins or honey by digestion, first with cold, strong alcohol, to remove the uncrystallizable sugar, and then expressing the residue, which is to be dissolved in water, and neutralized by chalk. The liquor so obtained may be clarified by white of egg, and evaporated to crystallization.

From starch, gum, or cane-sugar, it may be prepared by the action of sulphuric acid as follows: one part of potato-starch is to be boiled with four parts of water and $\frac{1}{50}$th of oil of vitriol during 36 or 40 hours, the water which evaporates being replaced. The jelly does not assume any consistence; the liquor remains clear, and the material used is found completely converted into sugar. By means of chalk, the acid is removed, and the solution being evaporated, the sugar crystallizes.

If starch paste be moistened with an infusion of pale malt, it is rapidly converted into dextrine, and thence into grape-sugar. This occurs from the catalytic influence of a principle termed *Diastase*, which exists in the malt, and the formation of which will be detailed under the head of germination.

To convert lignine into sugar, bits of paper or linen are to be imbibed with their own weight of oil of vitriol, until they are converted into a uniform viscid mass, taking care that it shall not become hot; this is then to be diluted, and the liquor boiled for some time. The acid being then removed by chalk, the sugar is obtained pure, by crystallization, as in the former case.

Sugar of grapes crystallizes in hard colourless tables or in hemispherical grains, consisting of minute needles closely aggregated together; its specific gravity is 1·38; it is much sweeter than cane-sugar, and less soluble in water. When heated to 212°, it gives off two atoms of water, which it recovers when redissolved; but by a stronger heat it is changed into caramel. It is soluble in twenty parts of boiling absolute alcohol, and separates almost totally on cooling, in granular crystals, which contain alcohol combined. It

combines with bases, forming compounds analogous to those given by cane-sugar.

The composition of crystallized grape-sugar is $C_{12}H_{14}O_{14}$, or $C_{12}H_{11}O_{11}+3$ Aq. When fused at 212°, it becomes $C_{12}H_{12}O_{12}$, or $C_{12}H_{11}O_{11}$ +Aq. Its compound with chloride of sodium, which crystallizes in fine double six-sided pyramids, consist of $2(C_{12}H_{12}O_{12})+$Na.Cl.+ 2 Aq. With a solution of basic acetate of lead it gives a white precipitate, the formula of which is $C_{12}H_{11}O_{11}+3$Pb.O., corresponding to the crystallized sugar. The dry grape-sugar has evidently the same composition as the crystallized cane-sugar.

The kinds of sugar (glucose) derived from these different sources are not so really identical as has been generally supposed, since they are found to act differently upon polarized light. Grape-sugar, as contained in the grape-juice or in the juice of the flowering grasses, rotates the plane of polarization to the left; but if the juice be evaporated and the sugar crystallized, its molecular constitution is so totally altered, as that, when redissolved, it gives a rotation to the right. The starch-sugar, as well as cane-sugar, rotates also to the right, but in a much inferior degree to the starch-gum, which, as already mentioned, receives its name of dextrine from that quality.

As lignine, starch, gum, and cane-sugar all contain the same quantity of carbon (C_{12}), their transformation into grape-sugar consists evidently in the fixation of the elements of water; thus lignine, $C_{12}H_8O_8$ takes 4H.O., and 100 parts of sawdust have been found to give 115 of sugar; starch ($C_{12}H_{10}O_{10}$) takes 2H.O., and 100 parts of it usually yield 106. It has been remarked, that a certain quantity of *Mannite* is at the same time produced, besides sacchulmine.

Grape-sugar yields, when treated with dilute sulphuric acid, the same brown substances as cane-sugar; but if the sulphuric acid be concentrated, it forms with the elements of the sugar a peculiar acid termed the *Sulphosaccharic*. Sugar of starch or grapes is to be fused at a low heat, and $1\frac{1}{2}$ parts of oil of vitriol then well mixed with it. If the sugar be pure and the temperature be kept low, the product is not coloured. Its constitution is not rigidly determined, but its lead salt consists of $2(C_{12}H_{11}O_{11})+S.O_3+4$Pb.O.

In acting on grape-sugar, nitric acid gives rise to the same products, oxalic and saccharic acids, as cane-sugar; indeed, it appears probable, that, like the other strong acids, this also first changes the cane-sugar into glucose, and that the saccharic acid is really derived from the latter. On this view its formation is more easily explained; for as the dry glucose is $C_{12}H_{11}O_{11}$, and the saccharic acid is $C_{12}H_5O_{11}$, the oxygen of the nitric acid simply removes six atoms of the hydrogen of the grape-sugar, and the elements of the acid remain.

By contact even with the strongest bases, cane-sugar is but slowly altered, and hence lime may be employed to clarify the vegetable juices which contain it; but, under the same circumstances, grape-sugar is rapidly decomposed and an acid formed, which is termed *Glucic Acid.* It is very soluble in water, and does not crystallize; with lime, barytes, and lead, it forms neutral soluble salts, but it precipitates a solution of basic acetate of lead. Its taste is purely acid,

and it reddens litmus. Its composition is $C_{12}H_8O_8$, and it is isomeric, therefore, in its dry state, with lignine. When a strong solution of caustic potash is added to fused grape-sugar boiled, the glucic acid which at first forms is decomposed. The liquor becomes deep brown, and yields, on the addition of muriatic acid, a black flocculent precipitate of *Melassic Acid.* The formula $C_{24}H_{12}O_{10}$ has been assigned to it, but its nature is not well known.

Lactine, or Sugar of Milk.—This remarkable substance, which is found only in the milk of the mammalia, is obtained by evaporating whey to a pellicle and setting it aside to cool, when the sugar crystallizes in small square prisms, white, semi-transparent, hard, and gritty under the teeth. The taste of the crystals is but slightly sweet, but that of a strong solution is much more so. It dissolves very slowly in water, and is insoluble in alcohol.

When the crystals of lactine are gradually heated to 270°, they give off two atoms of water; at about 300° they fuse, and give off three atoms of water more. The composition of the dry sugar thus obtained is $C_{24}H_{19}O_{19}$, and of the crystals $C_{24}H_{19}O_{19}+5$ Aq. By mixing solutions of sugar of milk and of basic acetate of lead, a white precipitate is produced, the formula of which is $C_{24}H_{19}O_{19}+5Pb.O$.

By digestion with dilute sulphuric acid, sugar of milk is changed into grape-sugar, and then produces the other reactions already described. With alkalies the decomposition is also the same as that of glucose, but the action of nitric acid on lactine differs from that on any other sugar, as the acid formed is not the saccharic, but that already noticed as obtained from native gum, the *Mucic Acid.*

To obtain mucic acid, one part of gum or lactine is to be dissolved in four parts of nitric acid, specific gravity 1·42, mixed with one part of water. Heat is to be applied until all effervescence has ceased, and the mucic acid is deposited on cooling. It is a crystalline powder, gritty under the teeth, and feebly acid. It dissolves in six parts of boiling water, but is insoluble in alcohol. Its crystals have the formula $C_{12}H_{10}O_{16}$, being formed from gum by the simple addition of six equivalents of oxygen. This formula contains, however, 2 Aq., as it is a bibasic acid, and its salts consist of $C_{21}H_8O_{14}+2M.O$. The alkaline mucates are soluble, the earthy and metallic salts are insoluble in water.

When mucic acid is long boiled with water, its acid properties become much stronger, and it becomes more soluble in water and soluble in alcohol; it gradually returns from this state to its ordinary condition, even when combined with bases. If mucic acid be distilled at a high temperature, water and carbonic acid are evolved, and a sublimate forms in brilliant white plates, which are soluble in alcohol and water; $C_{12}H_{10}O_{16}$ give $2C.O_2$ and $6H.O.$, besides $C_{10}H_4O_6$, which is the formula of the hydrated *Pyromucic Acid.* This substance fuses at 270°, and is volatile at 290° without decomposition. Its salts contain one equivalent of base; those of lead, barytes, and silver are insoluble; those of the alkalies are very soluble in water.

With this acid a certain quantity of chlorine may be combined, forming *Chloropyromucic Acid,* $C_{10}H_3 . Cl_4O_5$, which is prepared by acting with chlorine on *Pyromucic Ether.*

Sugar of Mushrooms is deposited in rhombic prisms from the watery solution of the alcoholic extract of ergot of rye. They are insoluble in ether; they give oxalic acid by nitric acid, and undergo the alcoholic fermentation. Their composition was found to give the formula $C_{12}H_{13}O_{13}$, but little is known accurately of this variety of sugar.

Of Mannite and Glycyrrhizine.

These bodies are connected so closely with the true sugars, that, although wanting in the characteristic of forming alcohol by fermentation, they may be best described here.

Mannite, $C_6H_7O_6$, is found in manna, of which it constitutes the sweet principle. It exudes also from the bark of other trees, and exists in most mushrooms. It is produced by the decomposition of cane-sugar in certain cases. To obtain it, manna is digested in boiling alcohol, and the liquor filtered while very hot; on cooling, the mannite is deposited almost totally, and may be purified by repeated crystallizations. Its taste is slightly sweet; it is very soluble in water, and it crystallizes in brilliant white prisms of silky lustre. When heated gently, it fuses without losing

weight. With nitric acid it gives oxalic and saccharic acids. It does not appear to combine with bases.

If the unclarified juice of the beet or carrot root be kept at a temperature of 100° for some time, a tumultuous decomposition sets in, which is termed the *mucous fermentation.* All the sugar disappears, and the liquor is found to contain a large quantity of gum and of mannite, with a peculiar acid, which exists naturally in all the animal fluids, but especially in milk, and is termed the *Lactic Acid.* At the same time, carbonic acid gas is evolved, and the liquor contains ammonia. This reaction is too complex to be expressed in formulæ, but it may be noticed that one equivalent of dry cane-sugar contains the elements of two equivalents of lactic acid; while, by abstracting two atoms of oxygen from an equivalent of crystallized grape-sugar, the constituents of two atoms of mannite remain.

Lactic acid is most easily prepared by means of this mucous fermentation, but may be also obtained abundantly from sour whey, or the sour waters obtained in making wheaten starch. The acid liquor is to be neutralized by carbonate of lead, and the solution of lactate of lead evaporated until it is tolerably concentrated. It is then to be decomposed by sulphate of zinc, and the precipitated sulphate of lead being removed by the filter, the lactate of zinc may be obtained in large crystals, easily rendered quite pure by re-solution and crystallization. A solution of pure lactate of zinc being decomposed by water of barytes, lactate of barytes is obtained, which, with sulphuric acid, gives sulphate of barytes, and the pure lactic acid dissolves. The solution is to be placed in vacuo over sulphuric acid; it gives a sirup-thick liquor, which has the formula $C_6H_6O_6$ or $C_6H_5O_5+Aq.$, as it contains an atom of basic water; it tastes strongly acid. When heated to 480° it gives off water, and a white sublimate forms in brilliant white rhomboidal plates, which is *Paralactic Acid.* It is purified by solution in boiling alcohol, from which it crystallizes. The composition of this body is $C_6H_4O_4$; it fuses at 225°, and sublimes at 450°; it tastes very slightly acid, and dissolves but very slowly in water; the solution gives, when evaporated, only the sirupy liquid of the hydrated acid, and does not crystallize.

The lactic acid coagulates albumen; it mixes with milk when cold, but coagulates it when boiled. It forms monobasic salts, in which its formula is $C_6H_5O_5$. They are all soluble in water, and crystallize but imperfectly, except that of zinc, which forms brilliant white four-sided prisms, containing three atoms of crystal-water. The *Protolactate of Iron*, $C_6H_5O_5+Fe.O.+3\ Aq.$, may be obtained crystallized in small prisms of a greenish-yellow colour. The *Perlactate of Iron* dries into a reddish transparent mass like shell-lac. These last are used in medicine.

The lactic acid will be again noticed as a constituent of the animal system.

Glycyrrhizine.—This substance, which is found in the liquorice-root, and in some other sweet woods, is obtained by boiling the root or liquorice in water, and, after concentrating the liquor, adding thereto sulphuric acid. A white precipitate, containing the glycyrrhizine combined with sulphuric acid and albumen, is formed. This is to be washed with acid water, and then with pure water, and to be dissolved in alcohol, which leaves the albumen. The alcoholic solution is to be decomposed by carbonate of potash, which throws down the sulphuric acid, and by evaporating the filtered liquor, the sweet principle remains pure as a yellow transparent mass.

Its most remarkable property is that of combining very definitely with acids and bases, and with several neutral salts. Almost every acid precipitates a compound from a solution of glycyrrhizine. It expels the carbonic acid from the carbonates of potash, soda, and barytes, combining with the base, and it precipitates the solutions of most of the ordinary metallic salts. Neither the pure substance nor any of its compounds have been accurately analyzed.

CHAPTER XXI.

OF THE ALCOHOLIC AND ACETIC FERMENTATIONS—OF ALCOHOL, THE ETHERS, ALDEHYD, ACETIC ACID, AND OTHER BODIES DERIVED FROM IT.

An aqueous solution of pure sugar may remain perfectly unaltered for any length of time, if carefully excluded from the air. If the air have access, it is gradually decomposed, becoming brown and sour, but no alcohol is generated. If, however, the solution of sugar be brought in contact with any organic substance which is itself in the act of slow decomposition, then the particles of sugar participate in the change which is going forward, and carbonic acid and alcohol result.

The substance which is specially active in inducing this kind of fermentation is an azotized body termed *yeast;* but a number of animal and vegetable substances can also effect it. Blood, white of egg, glue, flesh, if they have begun to putrefy, are capable of exciting it; but the bodies of most practical importance in that respect are vegetable albumen and gluten. These bodies exist in all fruits and seeds, in greater or less proportion, but they differ in character, according to the plants they are derived from, nearly in the same way as the varieties of starch. I shall here only notice them as derived from wheat and from beans, as I shall have occasion to describe some other forms hereafter. If wheaten flour be washed with water in a linen bag, the starch passes off, and a tenacious paste remains, which consists of albumen and gluten mixed. They may be separated by boiling in alcohol, which dissolves the latter, and leaves the former behind. On mixing the alcoholic liquor with water, the gluten is precipitated, and may be collected and dried.

Vegetable Gluten so obtained is pale yellow, and forms, when soft, an adhesive mass, very extensive and elastic. Its solution in alcohol is thick-fluid when concentrated; insoluble in ether; it dissolves in acetic acid, and in alkaline solutions. It combines with the mineral acids, forming bodies very sparingly soluble in water, which are precipitated by adding the acid to the solution of gluten in acetic acid or in potash. If these solutions be mixed with solutions of earthy or metallic salts, precipitates are formed, which are compounds of the gluten with the metallic oxide.

In all these reactions, the gluten is accompanied by a slimy material, termed *Mucin,* which it is difficult to remove perfectly from the gluten; it is best effected by boiling with water, when the mucin remains dissolved. Its solution is precipitated by sulphate of iron and infusion of galls, but not by acetate of lead or corrosive sublimate.

Vegetable Albumen remains behind after the rough gluten has been boiled in alcohol. It is destitute of elasticity when softened, and dries to a hard white mass; it is moderately soluble in water, and its solution is coagulated by heat; it dissolves in alkaline liquors. Its solutions are precipitated by acids, except the phosphoric and acetic, and by all earths and metallic salts; these precipitates are white or coloured, according to the nature of the metallic oxide; with ferro-prussiate of potash and with

infusion of galls, the solution of vegetable albumen in acetic acid gives white precipitates.

Legumin.—This substance, which exists in pease and beans, possesses properties intermediate to those of the gluten and albumen of wheat. When powdered pease are diffused through water, the starch settles to the bottom, but the legumin is dissolved, and separates by evaporation, on the surface of the liquor, in mucous transparent pellicles. Its solution is not coagulated by heat; it is insoluble in alcohol. It dissolves in solutions of the vegetable acids, and is precipitated on the addition of a mineral acid. It dissolves in alkalies, and gives, with the earthy and metallic salts, compounds insoluble in water.

All these substances differ from most vegetable bodies, in containing a large quantity of nitrogen, and, in the latter case, sulphur, as a constituent. They leave behind, when burned, an ash consisting of phosphates of lime, magnesia, and iron, similar to the ash of animal substances. Indeed, an almost perfect similarity of properties exists between these bodies, and fibrine, albumen, and casein among animal products; in the case of casein and lupuline probably amounting to identity. In contact with air and water, these bodies enter spontaneously into decomposition, evolving carbonic acid and ammonia, and forming new products; and in this state of decomposition they superinduce the alcoholic fermentation on those particles of sugar which lie in contact with them. Hence, in fruits, the sugar may lie in contact with these vegeto-animal substances without any change occurring, as long as the investing membrane of the fruit-cells remains perfect; but if the fruit be crushed, so that the air have access, then oxygen is absorbed, the vegeto-animal body begins to putrefy, and the sugar is soon engaged in the decomposition. It is remarkable, that the necessity for oxygen is at the commencement of the decomposition: when the putrefaction of the albumen or gluten has once begun, it extends itself throughout its whole mass without requiring any farther action of the air.

The principles of the conservation of vegetable juices, by enclosure in vessels from which the air is excluded, can easily be understood from this, as well as the utility of such agents as sulphurous acid or sulphite of potash, which absorb any traces of oxygen that may be present, and prevent it from acting on the organic substance.

The general characters of these *natural ferments* being thus sketched, it is necessary to add the important facts of the history of *artificial ferment*, or *yeast*. This is nothing more than the decomposing mass of vegetable gluten or albumen produced in a previous fermentation. If the yeast be too old, that is, if all the vegeto-animal matters be already decomposed, its power of exciting action is destroyed; it is also destroyed by boiling, by alcohol, by many salts and acids, and, generally, by all those means which give to the albumen and gluten an insoluble form, and prevent their farther putrefaction.

When a solution of pure sugar is fermented by contact with a certain quantity of yeast, this last is found to be very much diminished in quantity, and to have totally lost its activity. On the contrary, if, in place of pure sugar, grape or currant juice, or an infusion of malt, be used, the quantity of ferment is found to be much increased, and to preserve all its power. In this case the albumen and gluten of the vegetable juices are themselves brought into the same train of decomposition as the added

portion of yeast, and thus form a new and larger quantity of active fermenting material. Thus, in a brewery, the quantity of yeast continually increases. If yeast be examined with the microscope, it is found to contain a vast number of minute globular bodies, possibly animalcules, which derive their nutriment from it; but recently some very unfounded attempts have been made to connect these globules essentially with the process of fermentation, by the idea that, in the process of nutrition, they absorbed the sugar, and that the products of fermentation were excreted subsequently by them. But this is shown to be absurd by the simple fact that the weight of the alcohol and carbonic acid is greater than the weight of the sugar.

The phenomena of the alcoholic fermentation are best observed on the clear-expressed grape-juice, kept at a temperature between 70° and 80°, in a lightly covered vessel. After a few hours a slight effervescence is observed, and the liquor becomes turbid, as if pipeclay were diffused through it. As the effervescence increases, the liquor becomes warmer, and the precipitate forms flocculi, on which the gas-bubbles are evolved, being thereby carried to the surface of the liquor, and falling down again when the gas-bubbles have broken. This circulation continues until the fermentation has ceased, when the precipitate collects at the bottom. The liquor no longer tastes sweet; it contains no sugar, but in place of it an equivalent quantity of alcohol. An infusion of malt does not so readily ferment as the grape juice, unless some yeast be first added. In its spontaneous fermentation, most of the gum and sugar which it contains passes into the mucous fermentation, while but little alcohol is formed. In the practical manufacture of malt-drinks and spirits, therefore, the worts are always set to ferment by the addition of a suitable quantity of the yeast formed in a preceding operation.

Although the essential character of sugar is to be capable of alcoholic fermentation, yet the different kinds of sugar enter on that process with unequal facility. The sugar of milk requires the presence of a very active ferment, and of an acid, by the influence of which it is changed into sugar of grapes. Thus milk does not ferment until it has become clotted and sour; the casein then acts as yeast, in superinducing the alcoholic fermentation. Indeed, no matter what kind of sugar is employed in this process, it is changed into grape-sugar before fermenting, as is shown by the action of the liquor upon polarized light. The grape-sugar, as dried at 212°, contains exactly the elements of two atoms of alcohol and four of carbonic acid, as $2(C_4H_6O_2)$ and $4C.O_2$ arise from $C_{12}H_{12}O_{12}$. As cane-sugar takes an atom of water to form grape-sugar, it follows that cane-sugar, in fermenting, should yield more than its own weight of carbonic acid and alcohol; and it has been ascertained by experiment that 100 parts actually give 104, while by theory 105 should be produced, consisting of 51·3 of carbonic acid and 53·7 of alcohol. This coincidence of numbers proves that these bodies are the only products. The influence of the yeast is, therefore, strictly what Berzelius terms *catalytic*, but its action becomes much more definitely intelligible by considering it as a case of the general principle expressed by Liebig, that motion (decomposition) may be communicated from the particles of one body (yeast) to those of another (sugar) by virtue of proximity, as described more fully in p. 235–237.

As farther details of the circumstances of the alcoholic fermentation

would vary with the nature of the liquor to be produced, whether it be for immediate drinking, as wine, ale, or porter, or for distillation, and as these lead to purely technical descriptions of the arts of brewing, &c., I shall not enter on them.

Of Alcohol and the Ethers derived from it.

When any saccharine liquor, which has undergone the alcoholic fermentation, is distilled at a gentle heat, a very volatile liquid passes over, which, by successive rectifications, may be deprived of most of the water which had been mixed with it. In various degrees of strength, and contaminated by minute traces of essential oils, characteristic of the plants from which the saccharine liquor has been obtained, it constitutes the *potato-spirit, brandy, malt-whiskey, arrack, rum,* &c., of commerce. In a still stronger form it constitutes the *spirit of wine*, or *rectified spirit,* the term alcohol being applied to it only when it is chemically pure. By mere distillation alcohol cannot be freed from all the admixed water, for which it exerts a strong affinity. When its specific gravity is reduced to 0·813 at 60°, in which state it still contains 8·2 per cent. of water, or exactly half an equivalent, its boiling point remains constantly at 172°, and it distils over unchanged. In the form of proof spirit of commerce, its sp. gr. is about 0·920, and it contains 48 per cent. of absolute alcohol; the rectified spirit containing about 83 per cent., and having the specific gravity 0·839 at 60° F.

To obtain real alcohol, or absolute alcohol, as it is generally termed, rectified spirit is to be distilled at a moderate heat from some substance having a stronger affinity for water; as lime, caustic potash, carbonate of potash, or chloride of calcium. Of these the last named should be preferred. The water of the spirit combines with the body used, and, forming a hydrate, the real alcohol distils over. The rectification should be conducted in a water-bath.

A singular mode of concentrating alcohol is founded on the fact that alcohol does not moisten the animal tissues, but corrugates, and rather abstracts water from them. Hence, if a bladder be filled with spirit of sp. gr. 0·820, containing 90 per cent. of alcohol, and if it be left for a few days in a warm room, the spirit will be found to have its sp. gr. reduced to 0·800, containing 97 per cent. of real alcohol. The water permeates the bladder, and evaporates from the outer side; but, as the alcohol does not moisten the bladder, it cannot get through, and consequently remains behind, freed from water.

The very ingenious way of obtaining alcohol, devised by Graham, by evaporation in vacuo with quicklime, has been described in p. 87.

Alcohol thus obtained anhydrous has a sp. gr. of 0·7947 at 60°; it boils at 168°; tne specific gravity of its vapour is 1601; it does not become solid even in the most intense cold; its taste is burning and dry upon the tongue, owing to its abstracting water from its tissue. It is highly inflammaole, and burns with little light. From its volatility, if some drops of it are poured into a jar of oxygen gas, its vapour forms a powerfully explosive mixture. It does not conduct electricity. It mixes with water in every proportion, contracts in volume, and evolves heat. The sp. gr. of spirituous liquors is therefore always above the mean sp. gr. of the alcohol and water they contain. The greatest condensation occurs with 54 volumes of alcohol and 50 of water; the mixture occu-

pies only 100 volumes, and its sp. gr. is 0·927, being a little denser than proof spirit.

The formula of alcohol is $C_4H_6O_2$, and its composition is,

4 equivalents of carbon,	=24·2	. . .	52·66
6 " " hydrogen,	= 6·0	. . .	12·90
2 " " oxygen,	=16·0	. . .	34·44
The equivalent of alcohol,	=46·2	. . .	100·00

This is confirmed by the products of its decomposition, and by the specific gravity of its vapour; for,

4 volumes of carbon vapour	. (843×4)=	3372·0
12 " hydrogen	. . (68·8×12)=	825·6
2 " oxygen	. . (1102·6×2)=	2205·2
Give four volumes of alcohol vapour	.	6402·8
Of which one volume weighs	. . . .	1600·7

It will be shown, however, that alcohol consists of ether united to water, and that its formula is $C_4H_5O.+Aq$. Its vapour is then formed by the union of

$$\left.\begin{array}{l}\tfrac{1}{2}\text{ volume of vapour of ether, } =1290\cdot6\\ \tfrac{1}{2}\text{ volume of vapour of water, } = 310\cdot1\end{array}\right\} 1600\cdot7.$$

The uses of alcohol in chemistry and pharmacy are numerous and important. It dissolves the caustic alkalies and most deliquescent salts, combining with them to form *alcoates*, which resemble very remarkably the *hydrates*. Thus, if dry chloride of calcium be dissolved in alcohol, the *alcoate* crystallizes by cooling in large transparent plates. By heat, these are decomposed, and also by contact with water, which expels the alcohol, and takes its place. The permanent and efflorescent salts are generally insoluble in alcohol, and may be even precipitated by it from their solution in water, the alcohol seizing on the water.

An important pharmaceutic use of alcohol is for the solution of the resinous principles of plants, in the preparation of tinctures and alcoholic extracts. The strength of the alcohol must in these cases be regulated by the nature of the substances to be dissolved. Sometimes rectified spirit, at other times proof spirit being more effectual.

The manufacture of alcohol is itself one of the most important arts; it is the basis, also, of the manufacture of vinegar, of the making of resinous varnishes, and various other processes. To the chemist it is specially of interest as the type of a very interesting group of organic bodies, and yielding by its decomposition a very numerous series of products, which are of great importance in science, in pharmacy, and in the arts.

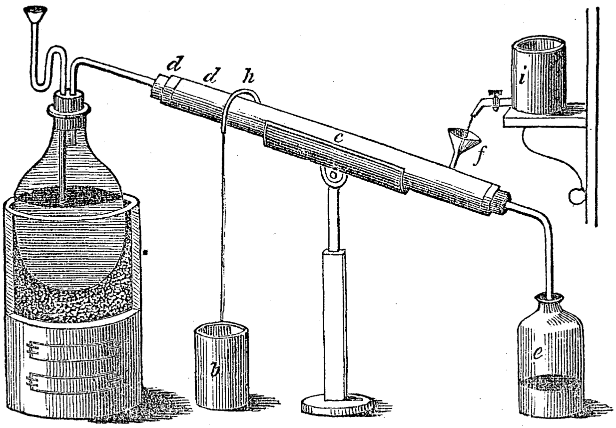
When alcohol is exposed to the air it gradually absorbs oxygen, aldehyd and acetic acid being formed. It is then said to undergo the *acetous fermentation*. Under the influence of acids it loses an atom of water, compounds being formed which are termed *ethers*, into the composition of which the acid employed generally enters.

Of Sulphuric Ether. Ether. Oxide of Ethyle.

This substance may be prepared by any process which deprives alcohol of the equivalent of water which it contains. Thus, if potassium be placed in contact with absolute alcohol, hydrogen gas is evolved, and a compound of ether and potash crystallizes, $C_4H_5O.+H.O.$ and K. giving $C_4H_5O.+K.O.$ and free H. If a current of gaseous fluoride of boron

(p. 326) be passed into alcohol, it is absorbed, and boracic acid separates in crystals, while the liquor contains ether; here, also, the water of the alcohol is decomposed, fluoric and boracic acids being produced, and ether liberated. By distillation with chloride of zinc, also, the water may be abstracted from alcohol, and ether obtained; but the affinity of the other deliquescent salts is not sufficiently intense to decompose it.

It is by the action of sulphuric acid upon alcohol that ether is, for practical purposes, always obtained. Equal weights of rectified spirit and of oil of vitriol being well mixed, and avoiding any considerable rise of temperature, are to be introduced into a glass globe, to which heat may be applied by a sand-bath, as represented in the figure. To this may be attached the form of condenser devised by Liebig for the distillation of very volatile liquids. It consists of a glass tube three



fourths or one inch wide, and twenty-four or thirty inches long, *d d*, to which is attached at one end by a good cork a narrower tube, passing to the globe, and to the other end is soldered a smaller tube, bent at an obtuse angle, and conducting to the receiver *e*. The tube *d d* fits water-tight by corks into a tinned cylinder *c*, the proportions of which may be judged from the figure; this is kept full of cold water. When the distillation commences, the hot vapours entering the condensing tube at *d*, give out their latent heat to the surrounding water, and that part of the condenser would soon get hot, were not the water constantly changed; by the funnel *f*, a stream of cold water flows from the reservoir *i* into the lower part of the tube *c*, and presses up before it the warm and lighter water, until this is expelled by the tube *h*, when it is collected at *b* The supply of cold water should be so proportioned to the supply of vapour, that, flowing away at *h*, it should not be sensibly warm to the hand. With this precaution, most volatile liquids may be perfectly condensed even in the midst of summer. The mixture of acid and spirit in the globe being brought to a temperature of about 260° as rapidly as possible, it begins to boil, and the ether distilling over, accompanied by some water and unaltered alcohol, collects in the receiver.

Since the quantity of sulphuric acid continually increases in the globe as the distillation proceeds, its action on the remaining alcohol changes,

the mixture becomes dark coloured, an oily substance distils over (oil of wine), and the quantity of ether formed diminishes rapidly. Sulphurous acid and olefiant gases are then evolved, and finally the mixture becomes thick and black, and froths up very much. When the object is only the preparation of ether, these reactions may be prevented, and a much larger product obtained, by admitting to the globe, by means of the bent funnel, a continual but minute stream of rectified spirit. The action of the sulphuric acid is thus exercised upon successive quantities of spirit, and the liberation of the ether continues until the acid becomes so weak as to be no longer able to decompose the alcohol, which occurs when the whole quantity of rectified spirit used is about twice the weight of the oil of vitriol, which is then reduced to the strength of $S.O_3+4$ Aq.

Although we may represent the results of this reaction by considering the sulphuric acid to take water directly from the alcohol, and set the ether free, such is by no means really the case; on the contrary, when the alcohol acts on the oil of vitriol, the water of both is disengaged, and the sulphuric acid and ether unite to form *Sulphate of Ether*, (C_4H_5 O.+Aq.) and $S.O_3$+Aq. giving $C_4H_5O.+S.O_3$ and 2 Aq. This body, which resembles very much sulphate of ammonia in its tendency to combination, unites with an atom of oil of vitriol to form *Bisulphate of Ether*, or, as it is generally termed, *Sulphovinic Acid*. The two atoms of sulphuric acid thus engaged change very much in properties, forming salts with barytes and oxide of lead, which are very soluble in water. The two equivalents of water, which, as above described, are set free, dilute the remaining sulphuric acid to such a degree as that it cannot decompose more alcohol; hence, if absolute alcohol be used, $3(C_4H_5O.+Aq.)$ with $8(S.O_3 . H.O.)$ produce $3(C_4H_5O. . S.O_3+H.O. . S.O_3)$ and $2(S.O_3+4$ Aq.). one fourth of the sulphuric acid remaining over; if a weaker alcohol be used, the quantity of dilute sulphuric acid formed becomes proportionally greater. An acid which already contains four atoms of water, forms no sulphate of ether when put in contact even with absolute alcohol, except the temperature be very high.

The ether obtained by distilling a mixture of alcohol and oil of vitriol results, therefore, not from the water being seized on by the oil of vitriol, but from the decomposition of its compound with sulphuric acid, the sulphate of ether; the ether being a base not much superior in energy to water, is expelled by it in turn under favourable circumstances, especially when the water is present in excess. In this respect it resembles, as Rose has remarked, the sesquioxides of iron, antimony, and bismuth, which form salts with sulphuric acid that are totally decomposed by a large quantity of water, especially if their solutions be boiled; the acid then combines with the water, and the metallic oxide precipitates. Before deciding on this view of the production of ether, it is necessary to describe some collateral phenomena.

If absolute alcohol and strong oil of vitriol be employed in the preparation of ether, it is found that the distilled product consists of ether and water, forming two distinct layers in virtue of their different specific gravities, but in quantity identical with those which constitute alcohol; 100 parts of the mixed liquids consisting of 19·5 water and 79·5 ether, when separated from a quantity of alcohol which had escaped decomposition. The oil of vitriol remains in the retort in its original state of concentration, and hence might be applied to etherify an infinite quantity

of absolute alcohol, introduced in a continuous stream. To explain this very remarkable result, Mitscherlich advanced that the action of the sulphuric acid on the alcohol is merely *catalytic;* that it splits it, as it were, into ether and water, and these pieces not being able to reunite, come over in vapour, merely mixed with each other; this idea is, however, quite inadmissible, as the whole quantity of ether is proved to be united with the sulphuric acid in the first place, and to distil over only after the decomposition of the compound that had been so formed. The observations of Liebig and Rose have removed the difficulty which this simultaneous evolution of water and ether presented to the adoption of the theory which supposes the ether to be expelled from its combination with the sulphuric acid by the water. In fact, it is only at a particular temperature that the ether and water come over in atomic proportions, and this then results from the identity of the boiling points of the solution of sulphovinic acid and of the dilute sulphuric acid. Thus, when we heat together sulphate of ether, ($C_4H_5O + S.O_3$), and the dilute sulphuric acid, $S.O_3 + 4$ Aq., the former is decomposed, bihydrate of sulphuric acid, $S.O_3 + 2$ Aq., being formed, and ether set free; but at this temperature the sulphuric acid begins to abandon its second atom of water, which then distils over with the ether. If we conduct the distillation very slowly, and retain the temperature below 212°, the ether comes over, almost perfectly free from water; but at a higher temperature, the ether, when liberated, is immediately converted into elastic vapour, which bubbles through the liquid like a gas, and the water evaporates in the space thus afforded, as it should evaporate in a current of air forced to bubble through the liquid in the same way.

The production of ether depends, therefore, upon the facts, that when alcohol and oil of vitriol are mixed, sulphate of ether is formed and water is set free; but on the application of heat, this action is inverted, and the ether is expelled from the acid, with which the water recombines. If the distillation be conducted so that the mixture boils, the dilute sulphuric acid concentrates itself, at the same time, by giving off an atom of water, which condenses mixed with the ether, but had its origin in a perfectly independent action.

If we heat alcohol in contact with glacial phosphoric or arsenic acids, it is similarly acted on, and the ether forms a *phosphovinic* or *arseniovinic* acid, which is decomposed by boiling, the ether being set free. These acids would be too costly to admit of their employment in the preparation of ether on the great scale, and, besides, they do not act as powerfully as oil of vitriol. Although this ether does not contain any sulphuric acid, it is very generally called *Sulphuric Ether*, and I shall often use that name, but the distinction between it and the compound ethers formed by its union with acids must be carefully kept in mind.

The ether formed by the process now described is rendered impure by admixture with alcohol and water, and sometimes oil of wine and sulphurous acid. It is freed from these by rectification, from a water-bath, over some dry carbonate of potash. It is then a colourless liquid, of an agreeable penetrating odour, and a pungent taste. Its sp. gr. is 0·720 at 60°; it does not conduct electricity; at —47° F. it freezes into a crystalline mass; it boils at 96°; the sp. gr. of its vapour is 2581·3. In evaporating it produces great cold, of which numerous applications have been noticed under the head of vaporization. (Sec. IV., Chap. III.)

Ether is very combustible; its vapour, diffused through air or oxygen, forms powerfully explosive mixtures. Exposed to the air, it gradually absorbs oxygen, forming acetic acid. Its flame is brighter than that of alcohol, but it gives no smoke; it dissolves sulphur and phosphorus in small quantity; iodine and bromine are abundantly dissolved, but they soon act on the ether; most bodies that are soluble in alcohol are dissolved by ether, except salts, of which only very few, as the perchlorides of gold, of platina, and of iron, are taken up by it. Ether combines with almost all acids, forming well-defined neutral salts, the *compound ethers*, which have a remarkable similarity to the ammoniacal salts. It is, therefore, an organic base; its composition is expressed in the formula C_4H_5O giving the numbers by weight:

4 equivalents of carbon	24·20	65·31
5 " " hydrogen	5·00	13·33
1 " " oxygen	8·00	21·36
	37·20	100·00

and by volume,

4 volumes of carbon vapour,	$(843\times4)=$	3372·0
10 " hydrogen "	$(68{\cdot}8\times10)=$	688·0
1 " oxygen "	$=$	1102·6
Produce two volumes of vapour of ether		5162·6
Of which one weighs, therefore		2581·3

In chemistry and pharmacy ether is of importance as a vehicle for the solution of many resinous and other bodies, and from its action on the animal economy. By the action of reagents it yields a great number of derived compounds, of which the most important will be described in their proper place.

The question of the intimate constitution of ether has been very much discussed, and opinions have followed precisely the same course, with regard to the theory of its compounds, as for that of the combinations of ammonia; thus it has been looked upon as an oxide of a compound (metallic?) radical, *Ethereum* or *Ethyle*, as the salts of ammonia were supposed to contain a compound metal, *Ammonium*. The formula of ethyle should be C_4H_5, and its symbol Ae. On the other hand, it may be considered to consist of olefiant gas, C_4H_4, united to water, and the latter then takes the place of the ammoniacal gas in the theory of ammonia. I shall frequently employ for ether the symbol Ae.O., and speak of it and other bodies as compounds of ethyle, as oxide, chloride, &c., but without any other present object than convenience of language, for it would be impossible to discuss the comparative merits of these theories, without knowing the properties of the compound ethers, of olefiant gas, of aldehyd, acetic acid, and many other bodies, which are involved in the reactions by which we may endeavour to test their value, and hence I shall postpone all details of the principles of the ether-theories until the end of the present chapter.

Compounds of Ether with Sulphuric Acid.

Sulphovinic Acid. Bisulphate of Ether, $C_4H_5O..SO_3+H.O..SO_3$, is produced by mixing alcohol with oil of vitriol, as described for the preparation of ether, or by passing vapour of ether into oil of vitriol as long as it is absorbed. By heat this solution is decomposed. The sulphovinic acid cannot be obtained in a solid form· if a solution of sulphovinate of lead be decomposed by sulphuret of hydrogen, a col·

ourless and very acid liquor is obtained, which, when concentrated, evolves ether, blackens, and is totally decomposed. Its salts are all soluble, and generally deliquescent; when boiled with muriatic acid, alcohol is evolved, and sulphuric acid set free. By a high temperature they are decomposed, oil of wine, ether, olefiant gas, and sulphurous acid being given off, while a metallic sulphate or sulphuret remains behind, mixed with some charcoal. By distilling a sulphovinate with a potash salt of any volatile acid, a compound of ether with that acid distils over, and sulphate of potash remains. By fusing a sulphovinate with a caustic alkali, water and olefiant gas are expelled, and all the sulphuric acid remains combined with the alkali.

Sulphovinate of Potash, $Ae.O..S.O_3+K.O..S.O_3$, crystallizes in colourless rhomboidal plates, which are anhydrous; it is very soluble in water, but sparingly soluble in alcohol. *Sulphovinate of Barytes*, $Ae.O..S.O_3+Ba.O..S.O_3+2\ Aq$, crystallizes in oblique rhomboidal prisms unalterable in the air; it tastes strongly acid, in vacuo it abandons its water, and is then not altered by a heat of 212°, but if the hydrated salt be heated to 212°, alcohol is given off, and sulphuric acid set free. *Sulphovinate of Lime* crystallizes in thin hexagonal plates, which are very deliquescent; it is soluble in less than its own weight of cold water. *Sulphovinate of Lead* forms large rhombic crystals, deliquescent; very soluble in water and in alcohol; it is gradually decomposed at ordinary temperatures. *Sulphovinate of Copper*, $Ae.O..S.O_3+Cu.O..S.O_3+4\ Aq.$, forms large blue octagonal plates, permanent in the air, and very soluble in alcohol and water; heated to 212° it is totally decomposed.

Ethionic and Isethionic Acids.—These substances are formed by acting on alcohol or ether with the vapours of anhydrous sulphuric acid; the liquor, neutralized by barytes, gives the insoluble sulphate and the soluble ethionate of barytes, which last separates from the concentrated liquor as a crystalline precipitate on the addition of alcohol. A solution of this salt, when decomposed by sulphuric acid, gives free *Ethionic Acid*, which, by boiling, is decomposed into sulphovinic acid and isethionic acid, of which, indeed, Liebig considers it to be, in reality, only a mixture. The isethionic acid is formed more characteristically by the direct union of anhydrous sulphuric acid and olefiant gas, and will be described as a compound of that body.

Althionic and Methionic Acids.—When the mixture of alcohol and oil of vitriol, for making ether, has been distilled so far as that it has become black and begun to froth, it produces, when neutralized with bases, a series of salts, which, though having the same per cent. composition as the sulphovinates, differ very much from them in properties; thus the *Althionate of Lime* does not crystallize; the *Althionate of Barytes* crystallizes in fine needles, in place of the large plates of the sulphovinate; the *Althionate of Copper* is still more distinct, as its crystals are thin, acute rhombs, of a pale green colour.

If the ether, into which the vapours of sulphuric acid are passed, be allowed to grow hot, it becomes black, sulphurous acid is evolved, and an acid is formed different from any of the preceding; it is called the *Methionic Acid*, and is characterized by its barytes salt being totally insoluble in alcohol, and but sparingly soluble in water. When its salts are fused with caustic potash, merely sulphite of potash remains; the formula of the acid contained in the barytes salt is $C_2H_3\ .\ S_2O_7$. It evidently does not contain any simple combination of alcohol or ether.

Heavy Oil of Wine. Sulphate of Ether and Etherol.—$C_8H_9O.+2S.O_3$, or $Ae.O..S.O_3+C_4H_4\ .\ S.O_3$. When one part of rectified spirit is distilled with two and a half parts of oil of vitriol, a little ether passes over, followed by an oily yellow liquid and water, with much sulphurous acid. The oil is to be washed with a little water, and then dried in vacuo under a bell-glass, beside two cups, one of oil of vitriol and the other of caustic potash; the first absorbs the water and ether, and the last the sulphurous acid. This substance is then a thin oil, sometimes green and sometimes yellow; its odour aromatic and pungent; its specific gravity 1·133; when heated it begins to boil, but is rapidly decomposed, blackening and evolving sulphurous acid, and but little distilling over. It is scarcely soluble in water, but abundantly so in alcohol and ether. When boiled with water, or with an alkaline solution, sulphovinic acid is formed, and *Etherol* (*light oil of wine*) set free, which floats upon the surface.

The composition of this body is not absolutely constant. I consider it to be a mixture, in variable proportions, of true *Sulphate of Ether*, $Ae.O..S.O_3$, with *Sulphate of Etherol*, $C_4H_4\ .\ S.O_3$. I have found that when distilled with oxalate or acetate

of potash, with chloride or sulphuret of potassium, oxalic and acetic ethers, muriatic ether, &c., are generated, and, at the same time, etherol remains indifferent to these re-agents.

Another process for obtaining this heavy oil of wine consists in mixing dry sulphovinate of lime with its own weight of quicklime, and distilling at a heat not exceeding 520°. The oil which comes over mixed with alcohol is to be purified as already noticed.

Etherol and Etherine.—C_4H_4. The oil which is separated from the foregoing substance by hot water or by alkalies, divides itself generally, after some time, into a liquid and a solid portion; the first constitutes the *light oil of wine, Etherol.* It is pale yellow, and thick, like olive oil; its odour is aromatic; its specific gravity =0·921; it boils at 500°; at —35° it freezes. The *Etherine* forms hard, brittle, colourless prisms; it is tasteless; its specific gravity 0·980; it melts at 230°, and boils at 464°; it is soluble in alcohol and ether. The composition of both these bodies is the same, consisting of equal numbers of atoms of carbon and hydrogen, but their atomic weights are not known. It is very probable that the etherol is really a mixture of two other bodies; for when a saturated solution of chloride of zinc in alcohol is distilled, an oily liquor is obtained, which, by rectification, may be separated into two fluids, of which one, boiling at 212°, has the formula C_8H_7, and the other, which boils only at 570°, has the formula C_8H_9. A mixture of equal quantities of the two should have the composition assigned to etherol.

Liebig and Regnault have found the etherol obtained by alcohol and sulphuric acid to have the formula C_4H_3, so that it must be looked upon as an irregular mixture of several oils, which have not yet been obtained pure. The etherol, or *Ethereal Oil*, is employed to prepare *Hoffman's Anodyne Liquor*, being dissolved in a mixture of one part of ether and two of spirit of wine.

Compounds of Ether with the Phosphoric and Arsenic Acids.

Phosphovinic Acid. — $Ae.O.\,.\,P.O_5+2H.O.$ When concentrated tribasic phosphoric acid is dissolved in alcohol, great heat is evolved, and one atom of water replaced by an atom of ether. The acid salt thus formed may be obtained crystallized, but when its solution is heated strongly it is decomposed. It combines with two atoms of base to form the *Phosphovinates*, of which few are as yet well known. The barytes salt, $P.O_5+Ae.O.\,.\,2Ba.O.+12$ Aq., crystallizes in brilliant colourless plates, and is remarkable for being equally soluble in water at 32° and 212°, but three times more soluble in water at 104°.

Arseniovinic Acid, $As.O_5+Ae.O.+2H.O.$, is formed with arsenic acid and alcohol, like the body last described. Its salts have been but very slightly examined.

Compounds of Ether with the other Mineral Acids.

Muriatic Ether. *Chloride of Ethyle*, $C_4H_5Cl.$, is prepared by distilling a mixture of three parts of oil of vitriol, four of fused common salt, and two of absolute alcohol. The retort should be connected with two two-necked bottles, of which the first should be immersed in a vessel of water at 60°, and the second be surrounded by ice, or a freezing mixture. Some alcohol and common ether, which pass over, are condensed in the first bottle, while the muriatic ether is reduced to the liquid state only in the second. By digestion with some chloride of calcium it is rendered quite pure.

It is a colourless liquid, of a pungent garlic odour; its specific gravity =0·874; it boils at 52°; is neutral; sparingly soluble in water; it burns with a bright flame, green at the edges, and gives off muriatic acid gas. By passing through a red-hot tube, it affords equal volumes of olefiant and muriatic acid gases, or by heating with potash, it gives olefiant gas and chloride of potassium. Heated with alkaline salts, it yields compound ethers and alkaline chlorides. When muriatic ether is heated with potassium, Löwig states that chloride of potassium is formed and a light oily substance separates, which has the formula C_4H_5. It should be *Ethyle*, but so important an observation has need of verification. This

body is often called *light Muriatic Ether*, to distinguish it from *heavy Muriatic Ether*, which results from the action of chlorine on weak alcohol.

Hydrobromic Ether. Bromide of Ethyle, $C_4H_5Br.$, is obtained by distilling together two parts of bromine, one of phosphorus, and six of alcohol. There is first formed bromide of phosphorus, which instantly decomposes the water of the alcohol, and the nascent hydrobromic acid acting on the ether forms the hydrobromic ether. In properties it perfectly resembles the following body:

Hydriodic Ether. Iodide of Ethyle, $C_4H_5I.$, is formed by distilling iodine, alcohol, and phosphorus. It is a colourless liquid, of a pungent ethereal smell; its specific gravity $=1{\cdot}92$; it boils at 161°; it is abundantly soluble in alcohol. Heated with potash, it gives pure olefiant gas and iodide of potassium. The theory of its formation is the same as in the former case.

Hydrosulphuric Ether. Sulphuret of Ethyle, $C_4H_5S.$, may be formed by acting on muriatic ether with an alcoholic solution of sulphuret of potassium. It boils at 187°; it combines with sulphuret of hydrogen to form the following very remarkable substance:

Sulphur-alcohol, or *Mercaptan*, $C_4H_6S_2$, or $Ae.S.+H.S.$, which is obtained directly by distilling in a water-bath concentrated solutions of sulphovinate of lime and of potash saturated with sulphuret of hydrogen, $K.S.+H.S.$ and $Ae.O.\,.\,S\,O_3+K.O.\,.\,S.O_3$ producing $2K.O.\,.\,S.O_3$ and $Ae.S.+H.S.$; the mercaptan distils over, and sulphate of potash remains in the retort; it is a colourless, thin liquid, of an insupportable smell of onions; it boils at 96°; its specific gravity is $0{\cdot}84$; it dissolves in alcohol; is perfectly neutral; burns with a bright blue flame; and by cold, freezes into a crystalline mass. In constitution, it is perfectly analogous to alcohol, the oxygen being replaced by sulphur. When placed in contact with metallic oxides, water is formed, and a double sulphuret of ethyle and the metal produced. This occurs remarkably with oxide of mercury, whence the barbarous name given to this body by Zeize, from *Mercurium Captans*, and to its compounds of *Mercaptides*. That of mercury is a crystalline solid, fusible at 110°, and soluble in alcohol.

The properties of this body induced its discoverer, Zeize, to look upon it as a compound of hydrogen with a compound radical, which he called *Mercaptum*, which should be really the following compound. Its formula then became $C_4H_5S_2+H.$ He extended this view also to common alcohol, which he considers as $C_4H_5O_2+H.$; but his theory has met with very few supporters.

Thialöl. Bisulphuret of Ethyle, $Ae.S_2$, is formed by distilling a mixture of sulphovinate of lime and persulphuret of potassium. It is a limpid, oily fluid, with a strong garlic smell; it boils at 124°. Its solution in alcohol precipitates the salts of lead and mercury. By the action of nitric acid on these sulphurets of ethyle, acids are produced analogous to the sulphovinic, but which are not, as yet, accurately known.

The *Seleniuret and Telluret of Ethyle* have been formed, but do not require description.

Nitrous Ether. Hyponitrite of Ethyle.—$Ae.O.\,.\,N.O_3$. When alcohol and nitric acid are directly mixed, the action is very violent; heat is evolved, red fumes are copiously given off, and acetic, oxalic, and carbonic acids formed. Even when the acid is dilute, its action is very

complex; giving up two atoms of oxygen to one portion of the alcohol, it produces aldehyd, and acetic and oxalic acids, and it is only the hyponitrous acid thus produced that acts on the remaining alcohol, and, combining with the ether of it, forms the proper nitrous ether. To avoid these oxidized products, the best plan is to generate red fumes of hyponitrous acid, by acting on starch by nitric acid in a retort, and to conduct these fumes by a bent tube to the bottom of a two-necked bottle containing alcohol. They are copiously absorbed, and combine directly with the ether. From the second neck of the bottle a tube should pass to a condensing apparatus and receiver; enough of heat is evolved by the absorption of the red fumes to distil over the nitrous ether formed, which may be thus obtained quite pure.

Another process, which may now be considered as obsolete, consisted in distilling a mixture of oil of vitriol, nitrate of potash, and rectified spirit, by the heat of a water-bath, into a receiver cooled by snow. The nitric acid acted very violently on the alcohol, and the product was impure, and small in quantity.

Nitrous ether is a liquid, colourless or pale yellow, of a pungent odour of apples; it usually reacts acid from slight decomposition, but is neutral if quite pure; its specific gravity is 0·947; it boils at 61° Fah. Exposed to the air, it absorbs oxygen rapidly, and forms aldehyd, acetic and formic acids; at the same time, nitric oxide is given off. By contact with any strong base, it is decomposed, alcohol being set free, and a hyponitrite formed. A solution of this nitrous ether in spirit (*spiritus nitri dulcis*) is employed in pharmacy. It is prepared by distilling a mixture of one part of nitric acid and ten of rectified spirit, collecting the first seven parts which come over, and digesting them on a little dry carbonate of potash, to remove any traces of free acid. Its specific gravity should be 0·850. It may be prepared directly by dissolving one part of real nitrous ether in eight parts of spirits of wine.

Cyanogen Compounds of Ether.

Hydrocyanic Ether. Cyanide of Ethyle, Ae.Cy., is prepared by distilling a mixture of sulphovinate of potash and cyanide of potassium at a moderate heat. It is a colourless liquid, of a strong garlic odour; it boils at 179°, and is lighter than water; it is very poisonous.

Cyanuric Ether, $3Ae.O.+2Cy_3O_3+6$ Aq., is formed when the vapours of hydrated cyanic acid are passed into ether, as long as they are absorbed. After some time, the new compound separates in crystals, which are colourless prisms, destitute of taste and smell, soluble in water, and but sparingly soluble in ether.

Hydrosulphocyanic Ether appears to be formed by distilling sulphocyanide of potassium with sulphovinate of potash. It is a liquid heavier than water.

Compounds of Ether with the Acids of Carbon.

Carbonic Ether. Carbonate of Ethyle.—$Ae.O..C.O_2$. This ether can only be produced by an indirect process, the theory of which is not well understood. Metallic potassium or sodium is added, in small pieces, to oxalic ether, as long as a disengagement of carbonic oxide gas occurs; a thick brown mass is formed, which is to be distilled, the excess of metal being first destroyed by the addition of water; the carbonic acid distils over. It is a colourless liquid, of an aromatic smell, lighter than water. It boils at 260°; it is insoluble in water, but dissolves in alcohol; its alcoholic solution is decomposed by potash, alcohol and carbonate of potash being formed.

Carbonate of Ether and Water. Carbovinic Acid.—$Ae.O..C.O_2+H.O..C.O_2$. At one time it was considered that anhydrous sugar was actually bicarbonate of ether, $C_6H_5O_5=C_4H_5O.+2C.O_2$, and that the alcoholic fermentation consisted in the sep-

aration of these bodies, the nascent ether combining with water to form alcohol; but that idea is now inadmissible. The true carbovinic acid is prepared by dissolving caustic potash in absolute alcohol, and passing dry carbonic acid gas through the liquor as long as it is absorbed. A crystalline mass is formed of carbonate and *Carbovinate of Potash*, which last is dissolved out by cold alcohol; and this solution, being mixed with ether, deposites the salt, whose formula is Ae.O.. $C.O_2$+K.O.. $C.O_3$, in pearly plates, which are immediately decomposed by water into alcohol and bicarbonate of potash. The carbovinic acid is not known in an isolated form.

Oxalic Ether. Oxalate of Ethyle, Ae.O.. C_2O_3, is prepared by distilling one part of alcohol with one of binoxalate of potash and two of oil of vitriol. At first alcohol and common ether come over, but then a heavy fluid, which sinks to the bottom of the receiver. The portions last distilled are richest in product. It is rectified by another distillation from off a little litharge. It is a colourless oily liquid, denser than water, of a heavy but aromatic smell; it boils at 370°. In contact with water or bases, it is gradually decomposed into alcohol and oxalic acid. The sp. gr. of its vapour is 5077.

Oxalovinic Acid.—Ae.O.. C_2O_3+H.O.. C_2O_3. This acid is not known except in combination. It is produced by adding to a solution of oxalic ether in alcohol half as much potash as would suffice to decompose it. The *Oxalovinate of Potash* separates as a crystalline powder, being insoluble in alcohol. By an excess of base it is decomposed into alcohol and an oxalate. Its other salts do not require special notice.

Oxamethan.—Ae.O.. C_2O_3+C_2O_2Ad. When oxalic ether is acted on by water of ammonia, it is totally decomposed, alcohol and oxamide being formed, as already noticed. If a solution of ammonia in alcohol be used, but one half of the oxalic ether is decomposed, and the oxamide produced unites with the other half, forming a substance soluble in alcohol and water, and crystallizing in brilliant prisms and plates. It melts at 212°, and sublimes unchanged at 430°. Its solution in cold water does not precipitate lime-water, but if it be boiled alcohol is expelled, and the solution contains binoxalate of ammonia. By water of ammonia it is totally changed into oxamide.

Chloroxycarbonic Ether.—Ae.O.. $C.O_2$+C.O.Cl. This substance is formed by the action of chlorocarbonic acid gas on absolute alcohol. It is a colourless liquid, perfectly neutral, heavier than water, and boiling at 201°; sparingly soluble in water. It consists, or, at least, contains the elements, of an atom of carbonic ether and an atom of phosgene gas. When put in contact with water of ammonia, it is dissolved violently, and heat evolved, sal ammoniac and a peculiar substance termed *Urethan* being formed. The liquor is to be dried down, and the residue distilled in a dry retort with an oil-bath. The urethan passes over, and solidifies in the receiver to a crystalline mass resembling spermaceti. In it the chlorine of the preceding substance is replaced by amidogene, its formula being Ae.O.. $C.O_2$+C.O.Ad.; it consists thus of carbonic ether and carbamide in the proportion of one atom of each.

Sulphocarbonic Ether. Hydroxanthic Acid, Ae.O.. $C.S_2$+H.O.. $C.S_2$, is prepared by decomposing the xanthate of potash by dilute sulphuric acid. A milky liquor is obtained, from which, after some time, a heavy oil separates; it is to be rapidly washed with water, and dried by chloride of calcium. It is then pale yellow, slightly acid, inflammable, and burns with a blue sulphurous flame; it is decomposed by warm water into alcohol and sulphuret of carbon; it decomposes the alkaline carbonates, expelling the carbonic acid. Of its salts, that of potash is obtained directly, and from it the others. *Xanthate of Potash*, Ae.O.. $C.S_2$+K.O.. $C.S_2$, is formed by adding sulphuret of carbon to a warm solution of caustic potash in alcohol. On cooling the liquor, it deposites the salts in crystals, which are to be collected on a filter, washed with ether, and dried between folds of bibulous paper. The salts of lead, copper, &c., may be prepared by double decomposition; they are all yellow, whence the ordinary name of the acid.

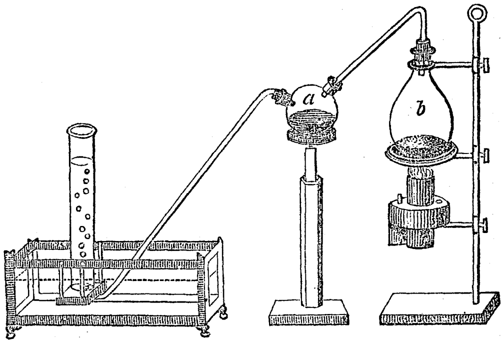
Mucate of Ether is solid and crystalline. It is formed by dissolving mucic acid in oil of vitriol, and gradually adding an equal weight of alcohol. The liquor yields, after some time, the mucic ether in crystals, which are to be dried on a porous stone, and recrystallized from alcohol.

The remaining compounds of ether with acids will be described along with the other salts of those acids.

Of Olefiant Gas and its Compounds.

This gas has been frequently mentioned as one of the products of the action of sulphuric acid on alcohol. The usual process to obtain it consists

in heating one part of alcohol with six of oil of vitriol in a flask, *b*, from which a tube passes to the water pneumatic trough, as in the figure; the mass becomes dark; ether, water, and oil of wine collect in the interposed globe, *a*, and olefiant gas is copiously evolved, mixed with an equal volume of sulphurous acid, which, however, being absorbed by the water, the other gas remains pure. Towards the end of the process the materials



in the flask swell up very much, and might boil over if not carefully attended to. The theory of this action appears, at first sight, very simple; the alcohol losing an atom of water, is first converted into ether, which, by the influence of the excess of sulphuric acid, is deprived of the elements of another equivalent of water, and olefiant gas remains, C_4H_5O. giving C_4H_4 and H.O.; but we cannot by this process generate the olefiant gas, without, at the same time, more complex products appearing, as etherol, sulphurous acid, and the black matter which remains in the retort. This last, which had been considered formerly as charcoal, appears to consist of $C_{27}H_8O_4+S.O_3$; it combines with bases, and is termed the *Thiomelanic Acid;* it evidently results from the sulphuric acid, giving up oxygen to the hydrogen of a portion of the alcohol.

Olefiant gas is generated on the large scale by the decomposition of coal, pitch, oil, &c., at a red heat, and is employed for the purpose of illumination, being the most valuable constituent of the gas which is burned in our streets and shops. To this source of it I shall have occasion to return.

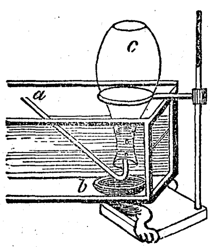
We may obtain this gas, however, by much more definite and simple processes. Thus, if vapour of muriatic ether be passed through a red-hot porcelain tube, it is resolved into equal volumes of olefiant and muriatic acid gases; also, if muriatic ether be heated with ammoniacal gas, sal ammoniac is formed, and olefiant gas evolved; the same decomposition is caused by caustic potash. If vapour of alcohol be passed into oil of vitriol so far diluted as to boil at 320°, and heated to that degree, it is totally resolved into water and olefiant gas. In a theoretical point of view, these sources of olefiant gas are peculiarly of interest.

Olefiant gas, when pure, is colourless; its odour is very slightly ethereal; it is sparingly absorbed by water; it burns with a brilliant white flame, producing much smoke. When mixed with twice its volume of chlorine, and set on fire in a tall narrow jar, a brilliant flame descends rapidly, muriatic acid being formed, and charcoal, smelling strongly of napthaline, separating in dense flocculi. Its specific gravity is 980·8, as one volume of it contains a volume of carbon vapour and two volumes of hydrogen (843·0+137·6=980·6). It consists of an equal number of equivalents of hydrogen and carbon, but chemists are not unanimous as to its real atomic weight. Berzelius, who looks upon it as an organic

radical, and the basis of a series of compounds with oxygen, chlorine, &c., has proposed for it the name *Elayl*, and the formula C_2H_2. The name *Olefiant Gas* being very inconvenient, I shall, in speaking of its compounds, term it, for the present, ***Etherene***. The principal support of the theory, which considers this gas to be the radical of the ethers and of alcohol, is derived from the great simplicity of their constitution by volume, in the state of vapour, on that view. Thus, two volumes of olefiant gas combine with two of vapour of water to form alcohol; with one of vapour of water to form ether; with two of muriatic or hydriodic acid gases to form the hydriodic or muriatic ethers, and so in similar simple proportions of volume in other cases. But this evidence is very insecure, as we might show nearly as simple gaseous relations upon other and very improbable points of view. Its combinations are generally formed indirectly, as from alcohol or ether, but it combines immediately with iodine, chlorine, and sulphuric acid.

Anhydrous sulphuric acid absorbs etherene in large quantity, forming white crystals, which, when dissolved in water, constitute *Isethionic Acid*, identical in every respect with that formed as described p. 546. When dry, its composition is $S_2O_6+C_4H_4$; but when in contact with water, it combines with two atoms thereof, and becomes isomeric with sulphovinic acid. That it differs from it essentially in constitution is shown by its salts giving a mixture of sulphate and sulphite when fused with potash; the sulphurous element is therefore as hyposulphuric, and not sulphuric acid, and its rational formula is $S_2O_5+C_4H_4O$. This isethionic acid is much more energetic than the sulphovinic; it decomposes all salts of organic acids; its own salts are all soluble and crystallizable, and sustain a heat of 450° without decomposition.

If a jar of olefiant gas, *c*, be inverted in the pneumatic trough, over a capsule, *b*, as in the figure, and bubbles of chlorine be passed up into it,



both gases disappear, and a heavy oily liquid collects in the capsule, the formation of which gave to the gas its common name of *Olefiant Gas*. In this process a quantity of gas is totally decomposed, and muriatic acid is evolved in great quantity, but the oil results from the direct union of the chlorine and etherene, its formula being $C_4H_4Cl_2$. I will name it *Chlor-etherene*, but it is called the *Oil of the Dutch Chemists*, as it was first formed by the members of a scientific association in Holland. When quite pure it is colourless, of a sweet ethereal odour. Its specific gravity $=1{\cdot}25$; it boils at 180°; it burns with a greenish flame, giving off muriatic acid; the specific gravity of its vapour is 3421. Exposed to an excess of chlorine, it is decomposed, hydrogen being removed, and replaced by chlorine; a volatile oily liquid, $C_4H_2Cl_4$, and ultimately *sesquichloride of Carbon*, C_4Cl_6, are produced.

The chlor-etherene is not decomposed by a watery solution of potash; but if it be dissolved in an alcoholic solution of that alkali, and gently warmed, chloride of potassium is formed, and a peculiar body produced, whose composition is expressed by the formula C_4H_3Cl. This substance is gaseous; of a garlic odour, burning with difficulty with a smoky red flame; its specific gravity is 2166. It is evident that the chlor-etherene may be considered as a compound of this gas with muriatic acid, C_4H

Cl.+H.Cl., in which case the action of the potash is easily explained. This gas itself is supposed to be a chloride of the same carbohydrogen as is the basis of acetic acid and aldehyd, (C_4H_3), or *Acetyl;* and the olefiant gas, on this view, is *Hydruret of Acetyl*, C_4H_3+H., or Ac.H. The farther discussion of this opinion will be reserved for another place. If the gas, C_4H_3Cl., be passed over perchloride of antimony, it combines with more chlorine and forms a liquid, which boils at 240°, and consists of $C_4H_3Cl_3$; by an alcoholic solution of potash this is decomposed into muriatic acid, and another body, also liquid, but boiling at 86°, and having the formula $C_4H_2Cl_2$. By contact with chlorine, this produces the liquid $C_4H_2Cl_4$, noticed in the preceding paragraph, as obtained directly from chlor-etherene, and, as the next stage, the sesquichloride of carbon.

If a mixture of olefiant gas and vapour of ether be acted on by chlorine, an oily liquid is obtained, which boils at 350°, and consists of C_4H_4 . Cl.O.; it is called *Chlor-etheral*, but is properly a compound of aldehyd and the chlor-etherene, $C_4H_4Cl_2$+$C_4H_4O_2$.

Bromine combines with olefiant gas, with the same phenomena as chlorine, and gives rise to a similar series of compounds, which it is consequently unnecessary to detail.

Iodine absorbs olefiant gas abundantly, and forms a white crystalline substance, which melts at 180°, and may be sublimed if air be not present. It is soluble in alcohol, insoluble in water; its formula is $C_4H_4I_2$, but the products of its decomposition are not similar to those of the chlorine compound.

When bichloride of platinum is dissolved in alcohol, a very complex reaction occurs, and a substance is produced consisting of Pt.Cl.+C_2H_2. This body combines with the chlorides of the alkaline metals to form double salts. On Berzelius's view, the C_2H_2 being a compound radical (*Elayl*), may be supposed simply to replace the second atom of chlorine, and thus form an *Elayl-chloride* of platinum, which has the same power of forming double salts as the ordinary bichloride. They are thus (Pt.+El.Cl.)+K.Cl. and (Pt.+El.Cl.)+Na.Cl., &c.

Of the Products of the Oxidation of Alcohol, Aldehyd, Hypoacetous Acid.—Eq. 555·6 or 44·2.

It has been mentioned, in speaking of nitrous ether, that by the oxidation of alcohol we obtain a crowd of products, as aldehyd and acetic acid, formic, malic, and oxalic acids; these last are secondary products of the too violent reaction, and the result of the true oxidation of alcohol is found to be aldehyd or acetic acid, according to the point at which the process stops. The formation of acetic acid thus directly from alcohol constitutes the *acetic fermentation.*

Although aldehyd is formed when nitric acid acts on alcohol, yet, from the other products being difficult to separate, it is not so prepared; a large quantity of it is generated in the destructive distillation of wood, and it may be obtained in the rectification of the pyroxylic spirit. The most ordinary process is that given by Liebig; six parts of oil of vitriol with four of water, four of spirit of wine, and six of black oxide of manganese, are to be distilled with a very gentle heat, and the product collected in a receiver surrounded with melting ice. The apparatus described for preparing ether (p. 542) should be employed. The process is completed as soon as the materials in the retort cease to froth up. I have found a purer product to be obtained by distilling, at a very gentle heat, two parts of spirit of wine with three of bichromate of potash, three of oil of vitriol, and six of water; the last two being previously mixed and allowed to cool. To obtain the aldehyd absolutely pure, it is to be combined with ammonia, and the crystallized *aldehyd-ammonia* decom-

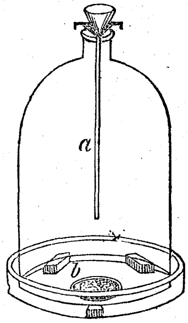
posed by dilute sulphuric acid, distilled in a water-bath at 120° with the greatest care, and rectified over fused chloride of calcium.

Aldehyd is a colourless liquid, of an agreeable but suffocating odour; it boils at 71°; it is lighter than water; it mixes with water, alcohol, and ether; it is neutral and inflammable, burning with a blue flame; in contact with oxidizing agents, it is changed into acetic acid, passing through an intermediate state of *Aldehydic Acid.* On this fact is founded its most characteristic property; if any liquor containing aldehyd be added to a solution of the ammoniacal nitrate of silver, and gently heated, the silver is deposited as a brilliant metallic film, lining the sides of the vessel like a mirror, and in the liquor is found aldehydate of silver; if to this potash be added, oxide of silver precipitates, and on boiling for a moment, it is reduced to the state of metallic silver, and acetate of potash is formed. From the composition of aldehyd, these changes are at once explained. It is formed by the abstraction of two atoms of hydrogen from alcohol, which are carried away, as water, by the oxygen supplied; its formula is hence $C_4H_4O_2$: now, in contact with Ag.O., it forms, first, aldehydic acid, $C_4H_4O_3$, and metallic silver, and then $C_4H_4O_3$ with Ag.O. gives hydrated acetic acid, $C_4H_4O_4$, and another quantity of silver. The formation of acetic acid from alcohol consists, therefore, in two stages; first, the abstraction of hydrogen, by which aldehyd is formed, and, second, the addition of oxygen, by which acetic acid is produced.

When aldehyd is heated in a solution of potash, this becomes brown, and by an acid a solid brown substance separates, which is fusible, and possesses many properties of a resin. This also is a very distinctive character of aldehyd.

When long kept, aldehyd undergoes an isomeric change into two bodies, one liquid, *Elaldehyd*, the other solid, *Metaldehyd;* they have the same formula as aldehyd, $C_4H_4O_2$, but differ in all their properties.

The general characters of aldehyd show that it contains the same radical as acetic acid, *Acetyl*, C_4H_3 or Ac., combined with oxygen; it is, therefore, *Hydrated Oxide of Acetyl*, $Ac.O.+Aq.=C_4H_4O_2$; it has been called, also, *Hypoacetous Acid*, for it is capable of perfectly neutralizing ammonia. Its compound with ammonia is, indeed, very remarkable; it is best prepared by dissolving aldehyd in ether, and passing ammoniacal gas into the liquor; the *aldehyd-ammonia*, being very sparingly soluble in ether, crystallizes as it forms in large hexagonal plates, which are very brilliant and colourless. Their solution in water soon decomposes, becoming brown, and exhaling an animal smell. The dry crystals may be fused and sublimed without alteration; their formula is $C_4H_3O.+H.O..N.H_3$.



Aldehyd is formed also by the direct action of the air on alcohol; this may be facilitated very much by means of spongy platina, which contains much oxygen condensed in its pores, but the process is of more interest in consequence of another body which then forms, and which cannot be otherwise generated; it is *Acetal.* To prepare it, a large bell-glass is taken, open above, and standing in a basin, so supported as to allow the air inside to be frequently renewed, as in the figure; through the top passes the tube of a small funnel, *a*, under which is a watch-

glass, *b*, with a layer of *platina black* (p. 407). Into the funnel strong alcohol is poured, so that from time to time a drop falls into the watch-glass; being thus presented to oxygen in a favourable condition, it is decomposed, and aldehyd, acetic acid, and *acetal* are formed. These liquids are vaporized by the heat evolved, but condense on the sides of the bell-glass, and, flowing down, collect in the basin underneath. By processes detailed in the systematic works, the acetal is purified. It is a colourless liquid, boiling at 200°; its odour is agreeable; its formula is $C_8H_9O_3$, and it appears to be a compound of aldehyd and ether, $C_4H_4O_2+C_4H_5O$.

The *Aldehydic Acid—Acetous Acid*—as already noticed, is formed by the partial oxidation of aldehyd; but it appears to be produced also under the circumstances of slow combustion, described in p. 179, along with acetic and formic acids. It is obtained pure by decomposing its silver salt by sulphuret of hydrogen, forming a liquor of an agreeably acid taste.

Of Acetic Acid. Vinegar.—Eq. 755·6 or 51·2.

As all alcoholic liquors are liable to undergo spontaneous decomposition, and form vinegar, this acid has been known from the earliest ages as produced by the *acetous fermentation;* its origin was, however, long wrapped in obscurity, for the complex constitution of the fermented liquors, in which it was ordinarily produced, prevented the simple nature of the change from being understood. It is now fully established, that the change from alcohol to acetic acid consists simply in the removal of two atoms of the hydrogen of the alcohol, and addition of two atoms of oxygen; these actions not being simultaneous, but successive, and aldehyd being the intermediate product, thus:

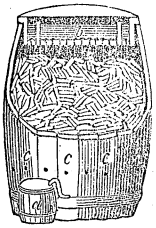
Alcohol, $C_4H_6O_2$,	and	Aldehyd, $C_4H_4O_2$,
gives by $-H_2$,		gives by $+O_2$,
Aldehyd, $\overline{C_4H_4O_2}$.		Hydrated Acetic Acid, $\overline{C_4H_4O_4}$.

By means of chromic and nitric acids, but especially by the platinum black as described just now, this reaction may be carried on with perfect accuracy and distinctness.

But if we place ourselves in the actual condition of practice, the theory of the acetous fermentation becomes much more difficult; for exactly as a pure solution of grape-sugar will not break up into alcohol and carbonic acid, and a cause of disturbance is necessary in order to enable the new arrangement of its particles to occur, so do we find it to be in changing alcohol into acetic acid. Pure alcohol, whether weak or strong, absorbs no oxygen by mere exposure to the air, and hence forms no vinegar; it is necessary there should be another body more liable to decomposition (ferment), which, abstracting oxygen from the air for the purpose of its own decomposition, may confer upon the molecules of alcohol such instability of structure as will admit of, and cause the similar absorption of oxygen by them. The ferment, in decomposing, evolves water and carbonic acid; the alcohol evolves water only, but absorbs the oxygen from the air. The platinum black, in the process that has been described, supplies the place of the ferment. In making vinegar from malt liquors or from wine, they are placed in hogsheads partially full, and left more or less exposed to the air, according to circumstances. To supply oxygen, the air must have access; but if the air were very

rapidly renewed, a large quantity of the volatile aldehyd would be carried off. These solutions contain abundance of organic matter, proper for acting as ferment; and when the fermentation is complete, the products of their decomposition collect upon the bottom and sides of the vats, in a gelatinous mass, termed *mothers*.

The manufacture of wine or malt vinegar by the old process of mere partial exposure to the air in vats consumed much time, and is almost superseded by the German method, by which excellent vinegar may be made in thirty-six hours. A cask is to be filled, as in the figure, with wood shavings, and closed at the top by a pan, *b*, the bottom of which is perforated with a number of small holes, through which short threads are passed, to bring down the liquid more rapidly. The shavings, before being used, are well steeped in vinegar, which is itself one of the most active ferments. Below, at *c c*, is a circle of holes about half an inch in diameter, by which the air may enter, which then escapes above by a number of tubes, which pass through the pan, and are left white in the figure. If now we take a spirit containing about one part of proof spirit to four of water, and, having mixed with it $\frac{1}{1000}$th of honey or yeast, pour it into the pan above, it trickles down the orifices by the threads, and, spreading over the shavings, has its surface enormously extended. It absorbs oxygen very rapidly, and, having been warmed to about 75° before being poured in, its temperature soon rises to 100°; the interior being so hot, a current of air is established through the vessels, by which a constant supply of oxygen is kept up. According as the liquid passes down, it escapes through the pipe at the bottom, and is collected in the vessel *a*; when it has passed through three or four times, it is found to be converted into excellent vinegar, and the whole time occupied is only between twenty-four and thirty-six hours.



The manufacture of vinegar by the distillation of wood will be described in another place.

The vinegar of commerce has frequently its pungency and acidity increased by the addition of acrid herbs, as capsicum, and by sulphuric acid. To obtain it free from these impurities, it is redistilled. As, however, its volatility is about the same as that of water, it cannot be concentrated in that way, and hence the strong acetic acid must be obtained by the decomposition of its salts by a stronger acid. For this purpose, one part of acetate of soda, which has been dried at a gentle heat, is to be distilled with two parts of oil of vitriol; so much heat is evolved by the mixture, that a quantity of the acetic acid distils over spontaneously, and to complete the decomposition only a very moderate heat need be applied. In this process, $S.O_3+Aq.$ and $Na.O.+C_4H_3O_3$ give $S.O_3+Na.O.$ and $C_4H_3O_3+Aq.$ The acid which passes over generally contains some sulphurous acid, arising from its secondary action on the oil of vitriol; in order to separate this, it is rectified over some peroxide of lead, with which the sulphurous acid forms sulphate of lead. The liquid acetic acid which distils is then to be exposed to a cold of about 23°, and the crystals which form are to be separated from the liquid portion; these crystals are the *Protohydrate of Acetic Acid*, and in its most concentrated form.

Acetic acid may be prepared also by distilling acetate of lead with oil of vitriol, or by the destructive distillation of acetate of copper: by this last method an acid is obtained (*radical vinegar*) of an agreeable aromatic odour, from an admixture of *Acetone*. The acetate of potash is prescribed by the Dublin Pharmacopœia; but, as acetate of soda is found abundant and cheap in commerce, it is now exclusively employed.

The *Hydrated Acetic Acid*, when free from any excess of water, crys-

tallizes at 50° in large white plates, which do not again become liquid until heated above 60°; it is hence called *Glacial Acetic Acid;* its odour is very characteristic and pungent; its taste caustic; it blisters the skin; it mixes with water, alcohol, and ether, and dissolves camphor and essential oils, which solution constitutes the aromatic vinegar of the shops. When liquid, its sp. gr. is 1·063; but its specific gravity does not indicate its strength, as it increases according as water is added until it becomes 1·078, which is that of an acid containing 34 6 per cent., or three atoms of water; being a definite compound, $C_4H_3O_3+H.O.+2$ Aq. On farther dilution, the sp. gr. again diminishes, and an acid containing 64 per cent. of water has a sp. gr. of 1·063, the same as that of the most concentrated acid. The strength of any acetic acid may, however, be very simply found by immersing in it a weighed piece of white marble, and weighing it again when the acid has been completely neutralized; the loss of weight gives pretty accurately the quantity of acetic acid, as the atomic weight of Ca.O. . $C.O_2$ (50·5) is nearly the same as that of $C_4H_3O_3$ (51·2); of course, if the acetic acid be not pure, this method cannot be employed.

The formula of hypothetic dry acetic acid is $C_4H_3O_3$, and its equivalent =51·2. The acetate of water, $C_4H_3O_3+$Aq., consists of

4 equivalents of	carbon,	=24·20 . .	40·20
4 "	hydrogen,	= 4 00 . .	6·64
4 "	oxygen,	=32·00 . .	53·16
		60·20	100·00

The hydrated acetic acid boils at 240°. The specific gravity of its vapour is 2278, and is anomalous as showing that its equivalent volume is 3, in place of 4 or 2, as occurs with almost all other organic bodies.

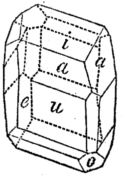
The products of the decomposition of acetic acid by chlorine and by bases will be hereafter noticed; with powerfully oxidizing bodies it yields formic, oxalic, and carbonic acids.

Acetic acid is recognised by its peculiar odour and its volatility; it reddens litmus powerfully; its solutions are precipitated by the nitrates of silver and of black oxide of mercury, giving white crystalline salts, sparingly soluble in cold water. But even strong solutions are not affected by the salts of lead or barytes. It combines with all bases forming salts, of which none are quite insoluble in water, but generally very soluble and easily crystallized. The most important of these *acetates* will now be described.

Acetate of Potash, K.O. . $C_4H_3O_3$, is formed by neutralizing acetic acid by means of pure carbonate of potash. The solution is generally evaporated at once to dryness, and the salt fused at a dull red heat, in order to obtain it quite white. It forms, on cooling, a foliated mass, greasy to the feel. From its concentrated solution it may be obtained, also, in delicate crystals. It is very deliquescent, and dissolves copiously in alcohol.

Acetate of Soda, Na.O. . $C_4H_4O_3+6$ Aq., may be obtained in the same way as acetate of potash, but is made on the large scale in purifying the rough wood-vinegar. The impure acetate of lime, obtained by neutralizing the pyroligneous liquors with chalk, is decomposed by $6\frac{1}{2}$ times its weight of crystallized sulphate of soda. These are in the proportion of two equivalents of Glauber's salt, as but one half of the quantity added is decomposed by the acetate of lime. It answers still better

to neutralize the acid liquors by sulphuret of sodium, prepared by roasting Glauber's salt with small coal, as for making soda-ash (p. 488).



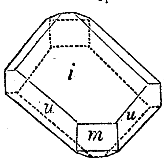
When purified by successive crystallizations, the acetate of soda forms oblique rhombic prisms, as *i*, *u*, in the figure, with many secondary planes, as *a*, *e*, *o*. These contain six atoms of water. It is permanent in the air; soluble in three parts of cold and in one of boiling water; at a red heat it melts. Its principal use is in the preparation of acetic acid.

Acetate of Barytes, Ba.O. . $C_4H_3O_3$, is formed by neutralizing acetic acid with carbonate of barytes or sulphuret of barium. It crystallizes in oblique rhombic prisms; by heat it is completely decomposed into carbonate of barytes and acetone (Ba.O. . $C.O_2$ and C_3H_3O.).

Acetate of Lime is made on the large scale, but in a very impure form, as one stage in the process of purifying the wood-vinegar. When pure, it crystallizes in needles, which do not deliquesce. It is decomposed by heat in the same way as the preceding salt.

Acetate of Alumina is of considerable technical importance, from its use as a *mordant* in dyeing. It is formed by mixing solutions of alum and of acetate of lead when to be employed in the arts. The solution then contains much acetate of potash. To obtain it pure, the simple sulphate of alumina should be decomposed by acetate of barytes. Evaporated at a very gentle heat, it dries into a transparent gummy mass; but if boiled, acetic acid passes off, and a *basic acetate of Alumina* is deposited as a white powder. This effect is produced also by contact with linen or cotton cloth, the acetic acid becoming free. A piece of calico is thus *mordanted* uniformly by immersion in a bath of acetate of alumina, and then dried at about 80°, or it is mordanted partially, so as subsequently to form a coloured pattern, by being printed with the solution of this salt, thickened with gum or starch, in order that it may not spread; on being then dried by passing over warm cylinders, the acetic acid passes off, and the alumina fixes itself upon the tissue.

Acetate of Zinc, Zn.O. . $C_4H_3O_3+3$ Aq. Metallic zinc dissolves in acetic acid, evolving hydrogen; but this salt is generally prepared by mixing solutions of acetate of lead and sulphate of zinc, and separating the sulphate of lead which is formed by filtration. On evaporating the solution, the acetate of zinc crystallizes in brilliant, soft, hexagonal rhombic tables, as in the figure, of which *i*, *u* are primary, and *m* a secondary face. They are unalterable in the air, but very soluble in water. When boiled with alcohol, a *basic acetate of Zinc* precipitates, 3Zn.O.$+C_4H_3O_3$. A solution of this salt is completely decomposed by sulphuret of hydrogen.



Protoacetate of Iron.—Fe.O. . $C_4H_3O_3$. This salt, which may be prepared by dissolving protosulphuret of iron in acetic acid, forms a colourless solution, which yields, when evaporated in vacuo, pale green prisms, which attract oxygen with great avidity It cannot be formed by decomposing protosulphate of iron by acetate of lead, as only a portion of the lead salt precipitates until the iron becomes peroxidized.

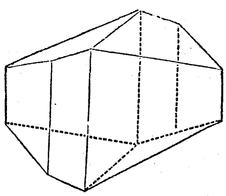
Sesquiacetate of Iron, $Fe_2O_3+3(C_4H_3O_3)$, is prepared by dissolving red oxide of iron in acetic acid, or by decomposing red sulphate of iron with acetate of barytes. It forms a brownish red solution, which, when boiled, gives off acetic acid, and oxide of iron separates. By very cautious evaporation, a dark red gummy mass may be obtained, which redissolves in cold water. It thus resembles closely acetate of alumina, and, like it, serves in dyeing as a mordant, to fix upon the cloth oxide of iron, with which the colouring matters may combine; being roughly prepared by

digesting old iron in the impure acetic acid from wood, it is commonly termed *Pyrolignite of Iron.*

A *tincture of Acetate of Iron* is employed in medicine, which, as directed by the Dublin Pharmacopœia, is formed by triturating together protosulphate of iron and acetate of potash, and digesting in alcohol; in order that the solution shall have the rich wine red colour which is required, the mixture of the salts should be left for a little time pasty, so as to absorb oxygen, and there should be present an excess of acetate of potash. The iron is present in these tinctures as black oxide. If too much sesquioxide be formed, the solution decomposes very easily, red oxide of iron separating, and acetic ether and aldehyd being produced. If the protoxide be present in excess, the colour is a brownish yellow, and the preparation is liable to spoil when oxygen has subsequently access to it. Although the acetate of potash does not form a true double salt in this case, yet it gives much greater stability to the acetates of iron.

Acetates of Lead.—Acetic acid forms, with oxide of lead, four well-characterized salts.

Neutral Acetate of Lead. Sugar of Lead, $Pb.O. . C_4H_3O_3+3$ Aq., is prepared by dissolving litharge, or white lead, in acetic acid, of which a slight excess should be used. The liquors yield by evaporation right



rhombic prisms with dihedral summits, as in the figure, which are very bright and colourless; their taste is sweet and astringent; the solution in water reddens litmus, but turns sirup of violets green. In very dry air they effloresce; when heated to 136° they undergo aqueous fusion, but, having lost their water of crystallization, become solid again. The dry salt thus obtained fuses again at a higher temperature, and without blackening, is decomposed into carbonic acid, acetone, and sesquibasic acetate of lead, which remains, $3(Pb.O. . C_4H_3O_3)$ giving $C.O_2$ with C_3H [illegible]. and $3Pb\ O.+2C_4H_3O_3$.

This neutral salt dissolves easily in alcohol; it is very poisonous; the antidote to it is Glauber's or Epsom salt, which forms insoluble sulphate of lead.

Sesquibasic Acetate of Lead.—$3Pb.O.+2C_4H_3O_3$. This salt, which is formed as just described, dissolves in water, and the sirupy solution crystallizes in pearly hexagonal plates; its solution reacts alkaline.

Tribasic Acetate of Lead.—$3Pb.O.+C_4H_3O_3$. When ammonia is added to a solution of neutral acetate of lead, so as to render it strongly alkaline, it does not combine with it as with most other metallic salts, but acetate of ammonia and tribasic acetate of lead are formed; it may also be prepared by boiling together six parts of crystallized acetate of lead, seven of litharge, and thirty of water. This solution, known in pharmacy as *Extractum Saturni,* gives, by evaporation, a mass of fine crystalline needles; it reacts powerfully alkaline; it is insoluble in alcohol.

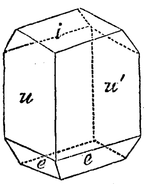
Sexbasic Acetate of Lead, $6Pb.O.+C_4H_3O_3$, is precipitated when a solution of neutral acetate is added to a great excess of water of ammonia; it is formed, also, when acetic acid acts on metallic lead with access of air, and is hence generally present in the *Ceruse* of commerce. (See

p. 491.) It forms minute feathery crystals when deposited from boiling water, in which it is slightly soluble.

All these basic acetates of lead are decomposed by carbonic acid, giving neutral acetate and carbonate of lead.

Acetates of Copper.—The acetate of the suboxide of copper is not important; there are four acetates of the black oxide.

Neutral Acetate of Copper. Distilled Verdigris, $Cu.O..C_4H_3O_3+Aq.$, is prepared by dissolving verdigris in acetic acid. It forms oblique rhombic prisms, as in the figure, where *i*, *u*, *u* are primary, and *e*, *e* secondary faces of a fine deep green colour. It crystallizes in another form with five atoms of water: these crystals are blue, like sulphate of copper, and when heated to 86°, give off 4 Aq., and change into the common green crystals; it effloresces gradually in the air; when heated in close vessels, it gives a mixture of acetic acid and acetone; in the air it takes fire, burning with a bright green flame.



If a solution of this salt be mixed with sugar or honey, and heated, it deposites a green powder of carbonate of copper, which changes into minute crystals of the orange-red suboxide: the liquor contains then abundance of formic acid.

Bibasic Acetate of Copper. Verdigris.—$2Cu.O.+C_4H_3O_3+6\ Aq.$ This salt is manufactured in wine countries by stratifying plates of copper alternately with the residual stalks and pulp of the grapes that have passed into acetous fermentation; oxygen is absorbed, and the mass being occasionally turned over and moistened, to give access to air, the plates of copper become covered with a crystalline crust of basic acetate; this is scraped off, made into a paste with vinegar, and put into moulds, where it is allowed to dry; the mass so formed contains all the basic salts mixed together. In this country it is prepared by stratifying copper plates with cloths steeped in pyroligneous acid. When pure, the bibasic acetate is of a fine blue colour; it is decomposed by water into the insoluble tribasic acetate, and the soluble *sesquibasic acetate* of copper, which forms a pale blue solution, whence it may be precipitated in crystalline scales by alcohol.

Tribasic Acetate of Copper, $3Cu.O.+C_4H_3O_3+2\ Aq.$, remains as an insoluble residue when verdigris is treated with water, or by digesting a solution of neutral acetate with oxide of copper. It is a clear green powder, which detonates feebly when heated. For *Emerald Green,* see p. 456.

Acetate of Black Oxide of Mercury, $Hg.O_2+C_4H_3O_3$, may be formed by mixing boiling solutions of acetate of potash and subnitrate of mercury, and filtering rapidly. On cooling, it is deposited in brilliant white crystalline scales, which are very sparingly soluble in cold water, and insoluble in alcohol. The *Acetate of the Red Oxide* is very soluble in water, and does not crystallize.

Acetate of Silver, $Ag.O..C_4H_3O_3$, is formed by mixing boiling solutions of nitrate of silver and acetate of potash, and filtering the liquor while very hot. On cooling, it crystallizes in pearly white needles, which are but very sparingly soluble in cold water. These last salts serve as tests for the acetic acid in liquids.

Acetate of Ammonia, $N.H_4O..C_4H_3O_3$, is prepared by passing ammo-

niacal gas over the crystalline hydrate of acetic acid, or by heating moderately a mixture of equal parts of acetate of potash and of sal ammoniac. The acetate of ammonia sublimes mixed with a little free acetic acid; it crystallizes in needles, which are very soluble in alcohol and in water; by exposure to the air it loses ammonia, and appears to form an acid salt; its solution in water, prepared by neutralizing distilled vinegar with carbonate of ammonia, is used in medicine by the name of *Spirit of Mindererus;* in its original form, when the carbonate of ammonia, obtained by the distillation of bones (*salt of hartshorn*), and which contained empyreumatic animal oil, was used, it was a much more powerful medicinal agent than when prepared, as now, with pure carbonate of ammonia.

Acetate of Ether. Acetic Ether, $C_4H_5O.+C_4H_3O_3$, is prepared by distilling 16 parts of dry sugar of lead, $4\frac{1}{2}$ of alcohol, and 6 of oil of vitriol; the product should be rectified over some lime to remove free acetic acid. This ether is colourless, and very inflammable; it boils at 165°; it is lighter than water; it is remarkable for being isomeric with aldehyd, their per cent. composition being the same, but the sp. gr. of the vapour of acetic ether (3063) is double that of aldehyd (1531).

Products of the Decomposition of Acetic Acid by Heat.

A. *Of Pyroacetic Spirit. Acetone.*

When acetate of lime or barytes is heated to redness, the acetic acid is completely decomposed, an earthy carbonate remaining, and a volatile inflammable liquid, of an agreeable aromatic odour, distilling over, $C_4H_3O_3$ separating itself into $C.O_2$ and C_3H_3O. The metallic acetates are similarly decomposed, but the products are not so pure. This liquid, for which I shall retain the name *Acetone*, is formed also abundantly when the vapour of acetic acid is passed through a tube containing charcoal, at a temperature just below redness.

Acetone is colourless, and lighter than water; it burns with a luminous flame; it boils at 132°; the specific gravity of its vapour is 2022. When heated with hydrate of potash, it is totally converted into carbonic acid and marsh gas, C_3H_3O. and $H.O.$ producing C_2H_4 and $C.O_2$. When treated by oxidizing agents, as permanganate of potash, or bichromate of potash and sulphuric acid, it is totally converted into acetic acid.

With sulphuric acid, acetone yields a series of products closely analogous to those derived from alcohol, but still presenting such characteristic differences as induce me to look upon them as not simply extracted from acetone, but derived from its total decomposition. Thus it gives a hydrocarbon, *Mesitylene*, whose formula is C_6H_4, and also an ether, *Mesitic Ether*, C_6H_5O. With sulphuric acid, this forms the *Sulphomesitic* and *Persulphomesitic Acids*, which are remarkable, as the sulphuric acid retains all its power of saturating bases. With phosphoric acid, it produces *Phosphomesitic Acid*, and with hypophosphorous acid a very remarkable compound, whose barytes salt has the formula $C_6H_5O.+2Ba.O..P.O.$ The series of wine-alcohol contains no similar body. The mesitic ether combines also with protochloride of platinum.

When acetone is treated with chloride of phosphorus, it gives phosphoric acid and *Chloromesitic Ether*, $C_6H_5Cl.$; with iodide of phosphorus it produces *Iodomesitic Ether*, $C_6H_5I.$; and, when acted on by chlorine, it forms, first, the *Mesitic Chloral*, of which the formula is $C_3H_2 . Cl.O.$, and subsequently another body, also a heavy, oily liquid, $C_3H.. Cl_2O.$

When red fumes of hyponitrous acid are passed into acetone, and the vessel is kept cool, they are copiously absorbed, and, on adding water, a dense fluid separates, which is *Nitrous Mesitic Ether*, $C_6H_5O.+N.O_3$.

By acting on mesitylene, C_6H_4, with nitric acid, a heavy liquid is produced,

4 B

which is termed *Mesitic Aldehyd;* its formula is $C_6H_3O.+Aq.$ Its solution in alkaline liquors becomes brown after some time, and precipitates most salts of the heavy metals. By chlorine, the mesitylene is converted into a crystalline body, soluble in ether, and separating from it in brilliant colourless prisms. Its formula is C_6H_3Cl. I have termed it *Chloride of Ptelcyl.*

In my original examination of this series of bodies, I looked upon acetone as an alcohol (*Mesitic Alcohol*), $C_6H_6O_2=(C_6H_5O.+Aq.)$, from which they were all derived; but I do not now consider that either mesitylene or mesitic ether pre-exists in acetone. The intimate nature of that body remains yet to be examined.

B. *Of the Bodies of the Kacodyl Series.*

When equal weights of acetate of potash and arsenious acid are mixed and distilled at a dull red heat, a dense colourless liquid is obtained, which had been long known to chemists as the *Fuming Liquor of Cadet.* The admirable researches of Bunsen have shown that it is an oxide of a compound radical, which he has succeeded in isolating, and which, in the variety of its combinations, and the influence their discovery will doubtless exercise on science, ranks with cyanogen. Nevertheless, as they are not of practical importance, a short notice of them will suffice.

The Fuming Liquor of Cadet, or *Alkarsine,* when purified from acetone and other accidental products of the distillation, is colourless; much heavier than water. It freezes at —9°, and boils at 300°. The specific gravity of its vapour is 7180; its odour is excessively disagreeable, provoking weeping and nausea; it is actively poisonous; in contact with the air it fumes very much, and absorbs oxygen so rapidly, that if a large surface be exposed, it takes fire spontaneously, and burns with a large white flame, throwing off much arsenious acid. Its composition is expressed by the formula $C_4H_6 . As.O.$, and in all the combinations which it gives, the oxygen alone is replaced. Thus, when distilled with strong muriatic acid, a dense liquid of an insupportable odour is produced, which gradually changes into a crystalline mass, consisting of $C_4H_6 . As.Cl.$ By digesting this liquid with zinc and water, in a vessel kept full of pure carbonic acid, chloride of zinc is formed, and the radical $C_4H_6As.$ is set free; this is an oily-looking, heavy liquid, insoluble in water, and taking fire immediately on contact with air. This is the *Kacodyl,* and as its symbol I shall adopt that used by Bunsen, $Kd.=C_4H_6As.$ The alkarsine is therefore oxide of kacodyl, Kd.O., and the body formed by muriatic acid is the chloride, Kd.Cl. The iodide, bromide, sulphuret, and cyanide of kacodyl, may be formed by the simple process of distilling alkarsine with the corresponding hydracids, or the chloride of kacodyl with the iodides, &c., of potassium.

When alkarsine is distilled with dilute muriatic acid, or when chloride of kacodyl is treated with water, this is decomposed, and an oxychloride obtained, the formula of which is Kd.O.+3Kd.Cl. In a similar manner, a corresponding oxybromide, Kd.O.+3Kd.Br., may be produced, and an oxyiodide.

If alcoholic solutions of oxide of kacodyl and of corrosive sublimate be mixed, a brilliant white precipitate is obtained, which is soluble in water, and crystallizes therefrom in large but delicate rhombic tables, of a satiny lustre. It is a direct combination, its formula being Kd.O.+2Hg.Cl. A precisely similar compound is formed with the bromide of mercury.

When alkarsine is exposed to the air, so that it may absorb oxygen, but not burst into flame, it is changed totally into a white crystalline mass; at the same time, arsenious acid and some volatile products are

formed. The crystals being dissolved in a small quantity of water, this liquor is evaporated to dryness, and the residue dried by blotting-paper, and recrystallized from alcohol. The substance thus obtained is termed *Alkargene;* it forms large oblique prisms, which are inodorous and tasteless; it deliquesces in moist air; it combines with alkalies and metallic oxides, forming very instable compounds; it melts at 390°, and is decomposed by a stronger heat. By deoxidizing agents, as protochloride of tin or phosphorous acid, it is reduced to the state of alkarsine; it is not poisonous. Its composition is expressed by the formula $C_4H_7 . As_, O_4$, or $Kd.O_3+Aq.$; its proper name is therefore *Kacodylic Acid.*

C. *Of light Carburetted Hydrogen. Marsh Gas.*

This gas is formed by the decomposition of almost every organic substance at a high temperature. Thus it exists always mixed with olefiant gas, in the coal or oil gas used for illumination. It may be formed by passing olefiant gas through a red-hot tube, when half of its carbon is deposited and its volume doubled. It is produced, also, by passing the vapours of alcohol, of ether, or of acetic acid through bright red-hot tubes in a similar manner.

A very interesting source of this gas is the decomposition of vegetable matter in contact with water, but excluded from the air. By assimilating the elements of four atoms of water, the lignine breaks up into carbonic acid and this gas, $C_{12}H_8O_8$ with $4H.O.$ giving $6C.O_2$ and $6C.H_2$. As the origin of the great deposites of coal is to be found in the slow decomposition of submerged forests of high antiquity, this gas was then generated in large quantity, and, being subjected to enormous pressure under the mineral strata, which gradually settled on the vegetable masses, it remained infiltrated through the coal, probably in a liquid condition. During the operations of mining, when this great pressure is removed, it reassumes its gaseous condition, and, mixing with the air of the mine, creates the danger of explosion, against which the genius of Humphrey Davy provided by the construction of his safety-lamp (see p. 183). Under the name of *Fire-damp,* this gas is known and dreaded by the miners, while the carbonic acid, which results simultaneously from the decomposition of the wood, and is known, also, from its fatal effects when breathed, is termed *Choke-damp.*

This decomposition of wood goes on in every muddy ditch. If the mud be stirred, numerous gas bubbles will be seen to ascend, and when collected will be found to consist of fire-damp mixed with carbonic acid; hence this gas has got the name of *Pond* or *Marsh Gas.* It is obtained, however, most pure by the decomposition of acetic acid by hydrate of potash. About equal parts of acetate of potash and caustic potash are to be well mixed, and heated in a hard glass retort nearly to redness. The acetic acid and water are simultaneously decomposed, $C_4H_3O_3$ and $H.O.$ producing $2C.H_2$ and $2C.O_2$. This last remains combined with the potash, while the gas which passes off may be collected over water.

It is colourless and transparent. It burns with a yellow flame, possessing but little illuminating power; its sp. gr. is 559; its formula being $C.H_2$, and consisting of

One volume of carbon vapour	=843·0
Four volumes of hydrogen	=275·2
Forming two volumes of marsh gas	1118·2
Of which one weighs, therefore	559·1

Or it may be considered as containing one volume of olefiant gas and two of hydrogen, condensed to two, $(980{\cdot}4+137{\cdot}6)\div2=559$.

The real atomic weight of the marsh gas is difficult to determine, as it does not form any well-defined combinations. There is reason to suppose it to be C_2H_4. When acted on by chlorine, it gives muriatic acid gas and bichloride of carbon (p. 498), which has been already noticed.

Of the Action of Chlorine on Alcohol, Aldehyd, Acetic Acid, and the various Kinds of Ethers.

When chlorine gas is passed into alcohol not absolutely anhydrous, a heavy oily liquid is obtained, known as *heavy Muriatic Ether* or *Chlorine Ether.* It is a mixture of several substances in indeterminate proportions.

When the alcohol is anhydrous and the gas quite dry, the action is definite, and gives rise to a remarkable result. Five sixths of the hydrogen of the alcohol are removed, and are replaced by three of chlorine, and, after the evolution of a large quantity of muriatic acid gas, a dense oily liquid is obtained, to which the name of *Chloral* has been given; its formula is $C_4H.\,.\,Cl_3O_2$. The first operation of the chlorine is to remove two equivalents of hydrogen, and thus to reduce the alcohol to the state of aldehyd, just as any other oxidizing agent should have done; but then it acts on the hydrogen of the radical, acetyl, and, expelling it, takes its place, generating a new compound radical, *Acechloryl,* C_4Cl_3. This is combined with oxygen and water in chloral, as acetyl is in ordinary aldehyd; the rational formula of chloral is therefore $C_4Cl_3O.+Aq$.

Chloral combines with water, forming a crystalline hydrate. It gradually changes into an isomeric porcellaneous-looking substance. The equivalent change of common aldehyd has been described (p. 554). When chloral is acted on by a solution of potash, it yields formic acid and chloroform, $C_4H.\,.\,Cl_3O_2$ and $H.O.$ giving $C_2H.O_3$ and $C_2H.Cl_3$.

By the action of chlorine on aldehyd, chloral is directly formed.

When the crystallized acetic acid is exposed to the action of chlorine in bright sunshine, a substance is formed which crystallizes in brilliant rhombs, and possesses strong acid properties; its formula is $C_4H.\,.\,Cl_3O_4$. It is formed by the replacement of the hydrogen of the radical acetyl by chlorine, forming thus the *Chloroacetic Acid,* $C_4Cl_3O_3+Aq$. Its salts crystallize with facility, and have great similarity to the acetates. When the chloroacetate of potash is heated with an excess of potash, it is decomposed into carbonic acid and chloroform; $C_4Cl_3O^3$ and $H.O.$ giving $2C.O_2$ and $C_2H.Cl_3$. This reaction is exactly similar to that of the common acetate of potash, the chloroform replacing the pond gas.

When chlorine acts upon sulphuric ether, a remarkable series of bodies is produced; the first formed is a dense oily liquor, having the formula $C_4H_3\,.\,Cl_2O.$, which, by contact with water or an alkali, is decomposed into hydrochloric and acetic acids, $3(C_4H_3\,.\,Cl_2O.)$ and $6H.O.$ producing $6H.Cl.$ and $3(C_4H_3O_3)$. This body is properly, therefore, *Oxychloride of Acetyl;* it is decomposed by sulphuret of hydrogen, muriatic acid being given off, and an *Oxysulphuret of Acetyl* being formed, which resembles it in properties.

In presence of a great excess of chlorine, this oxychloride is totally decomposed, the chlorine entering into the place of the hydrogen in the acetyl, and forming the same radical as exists in chloral and chloroacetic acid. The substance thus produced is solid and crystalline; it bears a very simple relation to sulphuric ether, as its formula is $C_4Cl_5O.$, being apparently ether, in which all hydrogen is replaced by chlorine. It may be termed *Chloryl Ether.*

The action of chlorine on the acetic and oxalic ethers has thrown much light on the theory of these bodies.

Acetic ether combines with two atoms of chlorine and loses two atoms of oxygen, thus giving from $C_4H_3O_3+C_4H_5O.$, the *Chloroacetic Ether,* $C_4H_3O_3+C_4H_3\,.\,Cl_2O.$, an oxychloride of acetyl, containing twice as much acetic acid as that just now described, and its rational formula being, therefore, $Ac.Cl_3+2Ac.O_3$; with potash it gives chloride of potassium and acetate of potash.

By a stream of dry chlorine gas oxalic ether is totally converted into a mass of crystalline plates, which are tasteless and perfectly neutral; this body contains no hydrogen, its formula being $C_6Cl_5O_4=C_4Cl_5O.+C_2O_3$. It is, therefore, a combina-

tion of oxalic acid with chloryl ether, and is termed *Chloroxalic Ether.* With water of ammonia it gives oxamide; by the action of dry ammonia it forms a substance also crystalline, which is soluble in alcohol and ether, sparingly soluble in water, and the formula of which is $C_8H_2Cl_5 . N.O_6$; at the same time, chloryl ether and water are evolved; the rational formula of this body, *Chloroxamethan,* is at once seen by comparing it with the oxamethan, formed by ammonia on oxalic ether (p. 550). Thus,

2 atoms of oxalic ether, $C_{12}H_{10}O_8$, give an atom of oxamethan, $C_8H_7 . N.O_6$.
1 atom of ammonia, $N.H_3$, gives an atom of alcohol, $C_4H_5O.+Aq$.

In like manner,

2 atoms of chloroxalic ether, $C_{12}Cl_{10}O_8$, give 1 of chloroxamethan, $C_8Cl_5H_2 . N.O_6$.
1 atom of ammonia, $N.H_3$, gives 1 of chlorine alcohol, $C_4Cl_5O.+Aq$.

The rational formula of the chloroxamethan is therefore $C_4Cl_5O..C_2O_3+C_2O_2Ad$.

When chloroxamethan is dissolved in water of ammonia, and the solution evaporated, crystals are obtained, which are *Chloroxalovinate of Ammonia*, their formula being $C_8H_4Cl_5 . N.O_8$, or, in its rational form, $C_4Cl_5O..C_2O_3+C_2O_3 . N.H_4O.$, identical in constitution with the ordinary oxalovinate of ammonia, except that it contains chloryl ether in place of common ether; the *Chloroxalovinic Acid* itself has been isolated; it crystallizes in long needles, which react acid, and combines with all bases to form well-defined salts; its formula is $C_4Cl_5O..C_2O_3+C_2O_3Aq$.

A crystallographic examination has rendered the isomorphism of the ordinary oxamethan with the chloroxamethan exceedingly probable.

The results of the action of chlorine on the light muriatic ether have led to remarkable results. Regnault considered this body as affording a test experiment for the actual presence of olefiant gas in ether; for if olefiant gas be Ac.H., and muriatic ether be Ac.H. . H.Cl., the result of the action of chlorine should be the same on both bodies, as the muriatic acid in the latter could not influence such a reaction Now, by acting on muriatic ether with chlorine, a series of bodies is obtained, isomeric with those arising from olefiant gas, but quite different in properties. Thus there is first formed a liquid, $C_4H_4Cl_2$; this has the composition of Dutch oil; next, a liquid forms whose formula is $C_4H_3Cl_3$; afterward, bodies consisting of $C_4H_2Cl_4$ and $C_4H\ Cl_5$, and ultimately C_4Cl_6, *Sesquichloride of Carbon.* Now the bodies $C_4H_4Cl_2$ and $C_4H_3Cl_3$, as derived from olefiant gas, are separated by potash into $C_4H_3Cl.$ with H.Cl., and into $C_4H_2Cl_2$ with H.Cl.; but the bodies $C_4H_4Cl_2$ and $C_4H_3Cl_3$, from muriatic ether, are not decomposed by that alkali. I do not, however, believe in the indefinite replacement of hydrogen by chlorine, which Regnault assumes, and look upon the relation of these series of bodies as being the following:

From Olefiant Gas.	From Muriatic Ether.
$C_4H_4Cl_2=C_4H_3Cl.+H.Cl.$	$C_4H_4Cl_2=C_4H_3Cl.+C_4H_5Cl.$
$C_4H_3Cl_3=2(C_2H.Cl.)$ and H.Cl.	$C_4H_3Cl_3.$
$C_4H_2Cl_4=2(C_2H.Cl_2).$	$C_4H_2Cl_4=C_4Cl_5Cl.+2(C_4H_3Cl_3).$
	$C^4H.Cl_5=C_4H_3Cl_3+2(Cl_4Cl_5Cl.).$

Both these give, finally, sesquichloride of carbon, C_4Cl_5Cl. The bodies from olefiant gas, which contain chloride of hydrogen, are decomposed by an alcoholic solution of potash, but those in which the chlorine is combined with an organic radical are not affected by that reagent.

By the action of chlorine on mercaptan, a similar series of products is obtained, of which the terminal body is $C_4H..Cl_4S.$, consisting of $C_4H_3S_3+2(C_4Cl_5Cl.)$.

On the Theoretical Constitution of Alcohol, and the Bodies derived from it.

The theory of alcohol and the ethereal combinations is of the more importance, as the principles of it regulate our ideas, not merely concerning the bodies that have been now described, but a vast number of others; for the ordinary, or *wine-alcohol,* is but one example of a numerous family of bodies, which resemble it in all its general laws of reaction, with, of course, peculiarities characteristic of each; thus wood-spirit, oil of potato-spirit, and ethal are alcohols.

The generic properties of an alcohol are, that its composition may be

represented by a hydrocarbon isomeric with olefiant gas, united with two atoms of water; that it gives an ether, which contains an atom of water less, and acts as a base; and that, by combining the hydrocarbon with four atoms of oxygen, an acid is formed. Thus we have,

	Wine-Alcohol.	Wood-Alcohol.	Oil of Potato-Spirit.	Ethal.
Alcohol,	$C_4H_4+2H.O.$	$C_2H_2+2H.O.$	$C_{10}H_{10}+2H.O.$	$C_{32}H_{32}+2H.O.$
Ether,	$C_4H_4+H.O.$	$C_2H_2+H.O.$	$C_{10}H_{10}+H.O.$	$C_{32}H_{32}+H.O.$
Acid,	$C_4H_4O.$	$C_2H_2O_4$	$C_{10}H_{10}O_4$	$C_{32}H_{32}O_4.$

Such being the connexion of the bodies of this class, the propositions in which I shall now proceed to imbody the principles of the constitution of the substances derived from wine-alcohol, may be hereafter immediately applied to illustrate the history of the other alcohols.

1. From the action of sulphuric acid, of chloride of zinc, of fluoride of boron, of potassium, and of chlorine on alcohol, it results that it contains an atom of water ready formed, united with sulphuric ether; its formula is therefore $C_4H_5O.+Aq.$

2. The sulphuric ether is a base, neutralizing the strongest acids, and producing both oxy-salts and haloid salts, perfectly resembling those of an alkali. The oxygen in ether may be replaced by all other electro-negative bodies, while the carbohydrogen, C_4H_5, remains constant. By the conditions laid down in p. 467, this, therefore, is a compound radical; it is called *Ethyl*, and its symbol is written Ae. Ether is oxide of ethyl, and its symbol is Ae.O.

3. By the action of oxidizing agents, hydrogen may be removed from ethyl, and a new radical, C_4H_3, produced, which, by combining with oxygen, forms aldehyd and acetic acid, its symbol being Ac. Aldehyd is protoxide, Ac.O., and acetic acid, peroxide of acetyl, $Ac.O_3$, both being considered free from water.

4. From olefiant gas, by the action of oxidizing agents, we cannot, in any case, pass to the series of bodies containing acetyl; nor can we, by bringing olefiant gas in contact with water or acids, produce any form of alcohol or ether. On the contrary, the isethionic acid is essentially distinct from these acids, which contain ether, and yields none by any form of decomposition; olefiant gas, on the other hand, gives, by the action of chlorine, a series of bodies, which are quite different from those given by muriatic ether, but which indicate that it is itself a radical, having laws of combination peculiar to itself, and independent, as Berzelius had already suggested, both of the alcohol and acetic series. Its formula is therefore C_2H_2; its symbol El.; and the Dutch oil is truly *Chloride of Elayl*. The ethyl may change itself readily into elayl by loss of hydrogen, since $C_4H_5=2C_2H_2$ and H., and it is thus broken up when the hydriodic or muriatic ethers are decomposed by heat, or by potash, or ammonia; or when sulphuric ether is acted on by an excess of sulphuric acid.

5. Although from the decomposition of ether we obtain olefiant gas, or light oil of wine, yet as ether cannot be in any way regenerated from these bodies by the influence of water or otherwise, neither can the other products derived from ether, as acetic acid, be produced from them, we must abandon the theory which considered ether to be a hydrate of C_4H_4, and consider it simply as an organic base, the oxide of ethyl.

6. By the action of chlorine on the ethereal compounds and on olefiant gas, radicals are generated, which are precisely equivalent to the

three, ethyl, acetyl, and elayl, but which contain chlorine in place of hydrogen. Their formulæ are C_4Cl_3, Cl_4C_5, and C_2Cl_2. This last is the protochloride of carbon, already described; the first, *Acechloryl*, exists in chloraldehyd and in chloroacetic acid; the second, *Ethchloryl*, exists combined with oxygen in chloryl ether, which acts as a base similar to common ether towards the oxalic and acetic acids. In contact with an excess of chlorine, it breaks up, as ethyl does, into olefiant gas and hydrogen, into the protochloride of carbon and chlorine, and thus the ultimate result is the sesquichloride of carbon, C_2Cl_3.

7. The series of bodies formed by the action of chlorine on elayl and on chloride of ethyl, are double combinations of bodies containing the hydrogen and chlorine radicals, and hence results their isomerism. Thus the body ($C_4H_2Cl_4$), from elayl, consists of $C_2H_2Cl.+C_2Cl_2Cl.$, while the body ($C_4H_2Cl_4$), from the muriatic ether, is really $2(C_4H_3Cl_3)+C_4Cl_3Cl_3$. The body, $C_4H_3Cl.$, from elayl, is $3(C_2H_2)+C_2Cl_2$.

8. The relation of acetyl to ethyl is simply that of internal constitution, described in p. 467. For as benzoic acid contains benzoyl, $C_{14}H_5O_2$, while this, again, contains, as radical, the carbohydrogen, $C_{14}H_5$, so ethyl, C_4H_5, contains within it, ready formed, the radical acetyl, and its formula might be still more correctly written as $Ac.H_2$. This is simply shown by the action of chlorine on ether, where $C_4H_3 . H_2O.$ becomes first $C_4H_3 . Cl_2O.$, and subsequently changes to $C_4Cl_3 . Cl_2O.$; the intermediate compound, $Ac.Cl_2$, relating itself to the oxygen, as the sulphurous acid, $S.O_2$, or the benzoyl, $C_{14}H_{15}O_2$, in the sulphuric and benzoic acids. Although the connexion of these two radicals is thus analogous to that of amidogen, Ad., and ammonium, $Ad.H_2 = Am.$, yet a broad line of distinction is drawn between the ammonia and ether theories, by the very definite character of ether, oxide of ethyl, as contrasted with the hypothetic oxide of ammonium; and, on the other hand, there does not appear to be any acetylide of hydrogen corresponding to ammonia, the amidide of hydrogen, for the assumption of olefiant gas as being that body is not based upon sufficient evidence.

Secondary Products of the Alcoholic Fermentation.

I have already noticed that, besides the carbonic acid and alcohol which are derived from the sugar, other bodies are evolved in minute quantities, and by their odour and taste characterize the spirit obtained from particular vegetables. Thus, in the fermentation of grape-juice, *Œnanthic Ether* is produced; in the spirit distilled from potatoes, a peculiar oil is found; and in the fermentation of malted corn, both of these bodies are generated, besides a third, to which the name of *Oleum Siticum*, or *Corn Oil*, has been given.

The *Œnanthic Ether* is a thin, colourless liquid, of an almost stupifying odour of wine, as to it the peculiar *bouquet* of wine is due; its specific gravity is 0·862; it boils at 445°; when heated with caustic soda, it evolves alcohol, and forms œnanthate of soda, from which the *Œnanthic Acid* may be separated by muriatic acid. This is a white crystalline solid, which melts at 88°, and distils over at 560° unchanged; its formula is $C_{14}H_{13}O_2$; it combines with water, forming a thick oil, which solidifies only at 55°, is tasteless and inodorous, but reddens litmus sensibly. The formula of the ether is $Ae.O.+C_{14}H_{13}O_2$; it is remarkable as the only ether that exists as a natural product, but it may also be formed artificially by means of alcohol and œnanthic acid.

The *Corn Oil*, of which the formula is $C_{42}H_{35}O_4$, is lighter than water, of a very penetrating odour, a biting taste, and cannot be distilled without partial decomposition.

The *Oil of Potato-spirit* has become of much interest, from the discovery that it gives rise to a series of ethereal combinations similar to those of wine alcohol; the name of *Amilic Alcohol* may be applied to it; it is colourless, oily, its odour at first

pleasant, but subsequently nauseous ; its taste acrid ; it burns with a blue flame its sp. gr. is 0·812 ; it freezes at 4°, and boils at 294° ; it dissolves in alcohol and ether ; its formula is $C_{10}H_{12}O_2$. In this alcohol a compound radical is assumed to exist, termed *Amilyl*, $C_{10}H_{11}$; its symbol is Ayl., and it is combined with oxygen and water, Ayl.O.+Aq., as ethyl is in wine-alcohol.

The *Amilic Ether*, Ayl.O., is not known except in combination with acids ; its bisulphate, or *Sulph-amilic Acid*, is obtained by acting on amilic alcohol with oil of vitriol; its formula is Ayl.O. . $S.O_3$+$S.O_3$. H.O. ; its barytes salt crystallizes in pearly plates, colourless, very soluble in water and alcohol. This salt is decomposed when its solution is boiled. The salts of lead and lime are completely similar in properties.

Chloride of Amilyl, $C_{10}H_{11}Cl$. or Ayl.Cl., is prepared by acting on amilic alcohol with chloride of phosphorus ; it is a colourless oil, which boils at 217°. By the action of bromine or iodine and phosphorus on the amilic alcohol, the *bromide* and *iodide of Amilyl* are prepared ; they possess properties similar to those of the chloride.

Acetate of Amilyl, Ayl.O.+$Ac.O_3$, is easily formed by distilling acetate of potash, oil of vitriol, and amilic alcohol ; it is a volatile, colourless liquid, which boils at 257°. The *Oxalate of Amilyl* may be similarly formed.

By distilling amilic alcohol with glacial phosphoric acid, a colourless aromatic liquid is obtained, having the formula $C_{10}H_{10}$. It is in this series what olefiant gas is in that of the wine-alcohol ; it is termed *Amilene ;* the sp. gr. of its vapour is 4918.

Valerianic Acid.—$C_{10}H_{10}O_4$. When the amilic alcohol is exposed to the air, it absorbs oxygen, but its oxidation is more rapidly effected by heating it with caustic potash. By a loss of hydrogen and absorption of oxygen precisely similar to that by which wine-alcohol forms acetic acid, it produces a volatile, oily acid, remarkable as naturally existing in the roots of the valeriana officinalis, and being extracted therefrom by distillation ; it is lighter than water ; it boils at 347°, and neutralizes bases, forming soluble sweet-tasted salts ; it must be considered as containing a radical analogous to acetyl, valeryl, $=C_{10}H_9$ or Vl., and its formula becomes $Vl.O_3$ +Aq.

When valerianate of lime is heated, carbonate of lime is formed, and a volatile liquid like acetone distils over ; it is termed *Valeron*, $C_{10}H_9O_3$ giving $C.O_2$ and C_9H_9O. The roots of the valerian contain, besides the valerianic acid, another oil destitute of active properties.

By cautiously treating amilic alcohol with sulphuric acid and chromate of potash, an oily liquid is obtained, which is *Valerianic Aldehyd*, $C_{10}H_{10}O_2$ or Al.O.+Aq. By an excess of chromate of potash it is changed into valerianic acid.

Treated with chlorine, the amilic alcohol, and the various amilic ethers, as well as the valerianic acid, give new products, which contain chlorine, and are constituted according to the same principles as have been fully described for wine-alcohol

CHAPTER XXII.

OF THE ESSENTIAL OILS, CAMPHORS, AND RESINS.

THE bodies now to be described constitute three groups, very closely allied in composition, in properties, and in origin. For the most part they exist ready formed in plants, as secreted by their proper organs, or they are derived, by reactions of a very simple kind, from substances so circumstanced. They are employed in medicine for their aromatic and stimulant properties, and in the arts for the manufacture of a variety of perfumes, varnishes, lacquers, &c.

A. *Of the Essential or Volatile Oils.*

These oils are so named from their solubility in alcohol, such solutions being called *essences*, and from their volatility. In virtue of this last prop.

erty, they are generally obtained by the distillation of the plants with water. If the oil were extracted by the distillation of the dry plant, the heat would rise so high as to destroy its odour and alter its composition; but, by using a large quantity of water, the mixed vapours of the oil and water pass over at a much lower temperature, as at 212°; for, although the boiling point of the oil may be 400°, yet it forms a quantity of vapour at 212° proportional to its tension at that degree. (See p. 78.) To prevent even the injurious heat which might arise from the plant touching the sides of the still, when fragrant flowers or leaves are operated on, they are suspended in a cage in the centre of the still, and allowed only to come into contact with the vapours. These oils are somewhat soluble in water, and, giving to it their odour and taste, form the various *medicated waters.* Hence often the same quantity of water must be distilled with fresh quantities of the plant before the oil is in such proportion as to separate.

Most essential oils, as those of turpentine, lemon, peppermint, &c., exist actually in the plant, as secretions from peculiar glands; but others are produced only at the moment of distillation, by the decomposition of substances which did exist in the plant, and which undergo a kind of fermentation. This is the case with the oils of bitter almonds, of spirœa, of mustard, and these oils possess much more active chemical properties than those of the former class. Another important difference among essential oils is, that some, by absorbing oxygen directly, produce well-characterized acids, as occurs in the oils of bitter almonds, of cinnamon, and of cloves; while others, as the oils of turpentine, citron, and copaiva, by a much more indirect action of oxygen, give origin to resins. On these principles I will arrange the oils in two classes, for convenience of description.

1st Class.—*Oils forming Acids not pre-existing in the Plant.*

Of Amygdaline and Oil of Bitter Almonds.

All plants which yield prussic acid on distillation produce, at the same time, a volatile oil, which is known as the *Oil of Bitter Almonds,* it being most abundantly obtained from that fruit. The leaves of the cherry-laurel, peach-kernels, &c., also yield it. The oil and the acid both arise from the decomposition of another substance, *Amygdaline.* This is prepared by bruising bitter almonds, and pressing them strongly between plates of hot iron, to force out the fixed oil; the residue is treated by alcohol of 93 per cent., and the solution evaporated in a water-bath to the consistence of a sirup; this is then diluted with water, and a little yeast added, which, by inducing fermentation, destroys a quantity of sugar. When this is over, the liquor is to be again evaporated to a sirupy consistence, from which the amygdaline is precipitated by the addition of cold strong alcohol, in which it is scarcely soluble; being dissolved in boiling alcohol, it is finally obtained pure by crystallization.

The formula of amygdaline is $C_{40}H_{27} . N . O_{22}$; it forms short silky needles, which are anhydrous, tasteless, and inodorous; it is very soluble in water, and crystallizes therefrom in large colourless prisms, containing 6 Aq. By contact with nitric acid it produces ammonia, oil of bitter almonds, benzoic and formic acids, and by caustic alkalies it is decomposed into ammonia and *Amygdalic Acid,* $C_{40}H_{26}O_{24} + Aq$.

When bruised bitter almonds are distilled with water, all amygdaline

disappears, and a number of products, as prussic acid and volatile oil, are evolved. Pure amygdaline may, however, be boiled in water without being altered. It is the animo-vegetal principle which constitutes the mass of the cotelydon of the almond that induces the reaction; it has been called *Emulsine*, and appears very similar in properties and constitution to the vegetable albumen or legumine, described as the active principle in the alcoholic fermentation. (See p. 538.) The emulsine is soluble in water, but insoluble in alcohol. If solutions of ten parts of amygdaline in 100 of water, and 1 of emulsine in 10 of water, be mixed, immediate decomposition occurs; the liquor becomes milky, smells of bitter almonds; it contains sugar, prussic acid, formic acid, and volatile oil, and the emulsine coagulates. It is most probable that the emulsine is itself also decomposed in this reaction, but we may explain the origin of these bodies from the amygdaline alone thus:

$$\left.\begin{array}{llll} 1 & \text{equivalent of} & \text{prussic acid,} & C_2H.N., \\ 2 & \text{"} & \text{volatile oil,} & C_{28}H_{12}O_4, \\ \frac{1}{2} & \text{"} & \text{sugar,} & C_6H_5O_5, \\ 2 & \text{"} & \text{formic acid,} & C_4H_2O_6, \\ 7 & \text{"} & \text{water,} & H_7O_7, \end{array}\right\} = C_{40}H_{27}\,.\,N.O_{22}, \text{ one equivalent of amygdaline.}$$

In the cotelydon of the almond, the amygdaline and emulsine are in distinct cells, and have no means of acting on each other, but when bruised in water both dissolve, and decomposition immediately occurs. The preparation of the oil by distillation can hence be fully understood.

The mixture of amygdaline and emulsine has been employed as a means of producing a prussic acid of standard strength for medicinal purposes.

Oil of Bitter Almonds. Hydruret of Benzyl.

Prepared by distilling bruised bitter almonds with water. In this rough state it contains a great quantity of prussic acid, from which it is freed by distillation with some water, chloride of iron, and lime. It is then colourless, of a strong peculiar smell, sp. gr. 1·043; it boils at 356°; when exposed to the air it absorbs oxygen, and forms crystals of benzoic acid; when heated with hydrate of potash, hydrogen is evolved, and benzoate of potash formed. The formula of this oil is $C_{14}H_6O_2$; but, from the series of compounds to which it gives rise, it is believed to contain an organic radical, $C_{14}H_5O_2$, termed *Benzyl*, and its rational formula is therefore Bz.H. (See p. 471.)

Chloride of Benzyl, Bz.Cl., is formed by acting on the hydruret with chlorine. It is a liquid heavier than water; it boils at 383°; when heated with water, it gradually changes into benzoic and muriatic acids. By heating chloride of benzyl with iodide of potassium, *Iodide of Benzyl* is formed; and by using the bromide, sulphuret, or cyanide of potassium, compounds of benzyl with these electro-negative bodies may be formed.

Amidide of Benzyl. Benzamide, Bz.Ad., is formed by acting on chloride of benzyl with dry ammonia, 2(H.Ad.) and Bz.Cl. give Bz. Ad. and Ad.H. . H.Cl.; it forms rhomboidal prisms, which melt at 240°, and may be distilled unaltered; heated with potash, it gives ammonia and benzoate of potash.

Oxide of Benzyl. Benzoic Acid.—Bz.O. + Aq. This acid is found ready formed in the resin of benzoin and in dragon's blood; it some-

times appears in the urine of herbivorous animals, and is formed by the oxidation of oil of bitter almonds and of amygdaline.

The following process for obtaining it pure was devised at the same time by Mohr and Hennell: 1 lb. of benzoin resin, in powder, is to be spread on the bottom of a metal dish, eight or nine inches diameter, and two inches deep, which is to be covered with a drum of blotting paper, pasted to the edge of the dish; the whole is to be covered with a cylindrical cap of stout packing paper. To render the heat uniform, the dish is to be placed on a metal plate, covered with sand, resting on a furnace; heat being cautiously applied for three or four hours, the cap is found full of splendid crystals of benzoic acid; the empyreumatic oil, which usually contaminates the sublimed product, being arrested by the drum of blotting paper, through which the vapour of the acid passes freely.

It may also be extracted from the resins by boiling these with lime; a soluble benzoate of lime is produced, from which the benzoic acid is precipitated by the addition of muriatic acid; it is then to be dissolved in boiling water, and allowed to crystallize by cooling slowly.

Benzoic acid crystallizes in hexagonal needles; when pure, it is inodorous; it reddens litmus feebly; melts at 248°; the fused acid boils first at 462°, but it sublimes freely at 293°; it dissolves in 25 parts of boiling water, but requires 200 parts of cold water for its solution; it is soluble in twice its weight of alcohol or ether; it forms a very extensive series of salts, of which few require special notice.

Benzoate of Lime, Ca.O. . Bz.O.+ Aq., crystallizes in brilliant prisms; at a dull red heat it is decomposed into carbonate of lime and *Benzone*, the formula of which is $C_{13}H_5O$. Another liquid, *Benzin*, $C_{12}H_6$, is at the same time formed by virtue of a much more complex process, napthaline, carbonic acid, and carbonic oxide being evolved.

Benzoate of Ammonia, Ad.H_2O. . Bz.O., crystallizes in brilliant plates. This salt is employed in mineral analysis to separate iron from manganese; a solution of peroxide of iron, not containing any excess of acid, being completely precipitated by neutral benzoate of ammonia, while the salts of manganese are not affected by it.

Benzoate of Silver, Ag.O. . Bz.O., is obtained by double decomposition; crystallizes from a boiling solution, on cooling, in brilliant colourless needles.

Formobenzoic Acid.—H.Bz.+Fo.O_3. If water, saturated with the impure oil of bitter almonds, be mixed with muriatic acid and evaporated, this substance crystallizes. The prussic acid is decomposed into formic acid and ammonia (p. 517), and the nascent formic acid combines with the hydruret of benzyl; in this body all the saturating power of the formic acid is preserved.

If a current of chlorine be passed through a solution of impure oil of bitter almonds in water, a similar body is formed, consisting of benzoic acid and hydruret of benzyl, Bz.H.+Bz.O.

Sulphobenzoic Acid.—$C_{14}H_8O_3+S_2O_5+2$ Aq. This body is formed by the action of dry sulphuric acid on benzoic acid. A viscid mass results, which, when neutralized by barytes, yields a salt permanent in the air, crystallizing in rhomboidal prisms, and having the formula $C_{14}H_8O_3+S_2O_5+2$Ba.O.+3 Aq. From this the pure acid may be obtained; it is decomposed if its solution be boiled, but when evaporated in vacuo it crystallizes. The sulphobenzoate of copper crystallizes in large rhombs of a rich blue colour.

Bromobenzoic Acid, $C_{28}H_9$. Br.O_3+2 Aq., is formed when benzoate of silver is decomposed by bromine. It is a crystalline solid, very soluble in water, fuses at 212°, and sublimes at 482°; its salts are all soluble, and contain two atoms of base.

Of the liquids produced by the distillation of benzoate of lime, *Benzone*, $C_{13}H_5O$, does not form any compounds; but *Benzin*, $C_{12}H_6$, produces with sulphuric acid,

nitric acid, and chlorine, a series of bodies, of which the formulæ alone need be here given ; they are,

Sulphobenzide,	$C_{12}H_5 . S.O_2$.	Chlorbenzin,	$C_{12}H_6Cl_6$.
Sulphobenzidic acid,	$C_{12}H_5 . S_2O_5$.	Chlorbenzid,	$C_{12}H_3Cl_3$.
Nitrobenzide,	$C_{12}H_5 . N.O_4$.	Azobenzid,	$C_{12}H_5N$.

I shall have occasion to refer to benzin as a product of the distillation of resin and coal. It is colourless, of an agreeable ethereal odour ; it boils at 187° ; its specific gravity is 0·85 ; that of its vapour is 2378 ; at 32° it freezes into a crystalline mass, which melts first at 43°.

Oil of Bitter Almonds with Ammonia.—By the action of water of ammonia on hydruret of benzyl, all oxygen is removed, and a crystalline body, *Hydrobenzamide*, produced ; its formula is $C_{42}H_{18}N_2$. It is soluble in alcohol, and by boiling the solution is decomposed into ammonia and hydruret of benzyl. The nitrogen here enters into the constitution of the radical, replacing the oxygen, and the body is *Hydruret of Azobenzyl* ($C_{14}H_5 . \frac{2}{3}N$)+H. This azobenzyl is itself also formed in the same process as the former, and also the *Azobenzoilic Acid* ($C_{14}H_5 . \frac{2}{3}N.$)+$\frac{1}{3}$N., which is benzoic acid, in which all oxygen is replaced by nitrogen. The origin of these bodies is explained by the constitution of the radical benzyl, as described in p. 471.

In the impure oil of bitter almonds a substance exists, termed *Benzoïne*, which is isomeric with the oil, its formula being $C_{14}H_6O_2$; it crystallizes in colourless prisms. By potash it gives benzoic acid and hydrogen ; by ammonia it forms a substance isomeric with *Hydrobenzamide.* By chlorine it gives muriatic acid, and in place of chloride of benzyl, a crystalline body, which is isomeric with that radical, its formula being $C_{14}H_5O_2$; this is termed *Benzoïl:* when heated with potash it gives the *Benzoïlic Acid*, which has the formula $C_{24}H_{11}O_5$+Aq.

By acting on oil of bitter almonds with a solution of sulphuret of ammonium in alcohol, Laurent has obtained a series of bodies, in which the oxygen of the radical benzyl is replaced by sulphur, and in some cases partly by sulphur and partly by azote ; there should thus be *Sulphobenzyl* ($C_{14}H_5S_2$), corresponding to the azobenzyl. It is unnecessary, in an elementary work, to enumerate the individual substances, but I look upon their formation as corroborating very much Berzelius's idea, that the true radical of the benzoic series is the carbohydrogen, $C_{14}H_5$, and that the chloride, &c., of benzyl are really oxychlorides, &c. (See p. 471.) Certainly the element which remains truly constant in those reactions (and hence satisfies the definition of a radical, p. 467) is $C_{14}H_5$, and not $C_{14}H_5O_2$.

Oil of Cinnamon and the derived Compounds.

This oil is found in the bark and flower-buds of the laurus cinnamomum and laurus cassia. It is heavier than water, and possesses the odour of the plant in the highest degree. It boils at 428° ; its formula is $C_{20}H_{11}O_2$, and for distinction I shall term it the α oil. When exposed to the air it absorbs oxygen, and forms another oil, which is that generally found in the shops, the β oil, the formula of which is $C_{18}H_8O_2$. Two resins, α and β, are at the same time produced.

$$\left.\begin{array}{c}\text{3 atoms of } \alpha \text{ oil}, =C_{60}H_{33}O_6, \\ \text{absorbing} \\ \text{6 atoms of oxygen}, =O_6,\end{array}\right\} \text{produce} \left\{\begin{array}{ll}\alpha \text{ resin}, & =C_{30}H_{15}O_4, \\ \beta \text{ resin}, & =C_{12}H_5O., \\ \beta \text{ oil}, & =C_{18}H_8O_2, \\ \text{5 atoms water}, & =H_5O_5.\end{array}\right.$$

The β oil of cinnamon, although thus only a product of the decomposition of the true oil, is very important, from the variety of compounds it gives rise to. It is heavier than water ; it dissolves in water of potash or of barytes, a *cinnamate* of the base being formed, and an oil lighter than water separating, $2(C_{18}H_8O_2)$ and H.O. giving $C_{18}H_{10}O_2$ and $C_{18}H_7O_3$. The properties of this oil indicate that it contains an organic radical, *Cinnamyl*, $C_{18}H_7O_2$, united to hydrogen. It is *Hydruret of Cinnamyl*, Ci.H., and the oil lighter than water is Ci.H_3.

Cinnamic Acid, Ci.O.+Aq., is formed by exposing the hydruret of cinnamyl to the air ; it absorbs two atoms of oxygen, and forms crystallized cinnamic acid. It forms colourless groups of plates of an acid taste ; it is almost insoluble in water, but easily soluble in alcohol and ether. It melts at 264°, distils over at 554° unchanged. Its salts are exceedingly similar to the benzoates.

Hydruret of cinnamyl combines directly with muriatic acid, with nitric acid, and with ammonia, forming compounds which are solid and crystalline. Their formulæ are Ci.H. . H.Cl., Ci.H. . H.Ad., and Ci.H. . H.O.+N.O_5. By chlorine one half of the hydrogen of this β oil is removed, and a white crystalline body formed, $C_{14}H_4 . Cl_4O_2$. The chlorine here enters into the constitution of the radical.

Oil of cinnamon combines with iodide of potassium and iodine to form a substance which crystallizes in large needles of a brilliant bronze colour, like permanganate of potash. Its formula is $Ci.H.I_3+K.I.$ Once formed, it is decomposed by water. It was discovered by Moore, of Dublin, and analyzed by Apjohn.

The origin of the *Balsams of Peru and Tolu* is closely related to the oil of cinnamon. They consist of resinous substances (the α and β cinnamic resins?), and of an oil which may be obtained pure by distillation. It is called *Cinnameine;* its formula is $C_{18}H_8O_2$, being isomeric with the β oil of cinnamon. It is neutral; but when its alcoholic solution is boiled with potash, it forms cinnamate of potash; or, by simple boiling of its alcoholic solution, *Cinnamic Ether* is produced, and another oil, *Peruvine,* is separated, the formula of which is $C_{18}H_{12}O_2$. In these cases three atoms of cinnameine and two of water produce two atoms of dry cinnamic acid and one of peruvine.

These researches on the nature of the balsams are due to Fremy; but Richter has advanced that the balsam of Peru contains two oils, which he terms *Myriospermine* and *Myroxyline,* the relation of which to peruvine and cinnameine is not yet established.

By the action of an excess of nitric acid, both oil of cinnamon and cinnamic acid are converted into oil of bitter almonds and benzoic acid.

Oil of Cloves, Eugenic Acid, &c.

The oil obtained by distillation from the undeveloped flower-buds of the eugenia caryophyllata is a mixture of several bodies. By the action of potash, it is separated into a volatile oil which does not possess active properties, is lighter than water, and consists of $C_{10}H_8$, while a eugenate of potash dissolves. From this solution the *Eugenic Acid* is precipitated by any strong acid.

Eugenic Acid. Heavy Oil of Cloves, $C_{24}H_{15}O_5$, is a colourless oil, sp. gr. 1·079; it boils at 470°; its taste and smell are those of cloves. It forms, with the metallic oxides, well-defined salts, most of which are soluble and crystallizable.

When the common oil of cloves is kept for some time, it deposites a crystalline substance, *Caryophylline,* $C_{20}H_{16}O_2$; it is soluble in alcohol, insoluble in water. It is volatile. From water distilled with cloves a different body separates in pearly scales, having the formula $C_{20}H_{12}O_4$. It is called *Eugenine.*

The eugenic acid and eugenine are rendered blood-red by contact with nitric acid.

The *Light Oil of Cloves* has sp. gr. =0·918; it boils at 287°.

Oil of Spiræa Ulmaria. Salicide of Hydrogen.

The oil distilled from the flowers of the meadow-sweet is a mixture of a light and of a heavy oil, with a solid body like camphor. The heavy oil is of much interest, from the number of compounds which it forms, and from our being able to form it at will, although from a body, salicine, which has not been found to exist in the spiræa. The impure oil of spiræa is purified by adding potash, by which the light oil is separated, and *Salicide of Potassium* formed, which, when acted on by sulphuric acid, yields the *Salicide of Hydrogen* pure.

To form it artificially, equal parts of salicine and bichromate of potash are to be distilled with 2½ parts of oil of vitriol and 20 of water. There is heat evolved and much gas disengaged; on then distilling, the heavy oil passes over. Two atoms of dry salicine ($C_{42}H_{24}O_{18}$), without any oxygen, might yield three atoms of oil, $3(C_{14}H_6O_4)$, and six of water; but the reaction is far more complicated in reality, as four parts of salicine yield but one of oil.

The properties of this oil show it to be a compound of a radical ($C_{14}H_5O_4$), *Salicyle,* Syl., with hydrogen; it acts as a hydracid in combining with metallic oxides; its specific gravity is 1·173; it boils at 380°. The specific gravity of its vapour is 4260. In this and in composition it agrees with crystallized benzoic acid, with which it is isomeric. The alkaline *Salicides* are soluble and crystallizable; those of lead, zinc, and mercury are insoluble. If a solution of any salicide be mixed with a solution of a sesqui-salt of iron, the liquor assumes a fine purple colour, by which the oil is well characterized.

When salicide of hydrogen is heated with caustic potash, hydrogen is evolved, and *Salicylic Acid,* Syl.O., formed; the potash salt being dissolved in water, and muriatic acid added, the new acid is precipitated, and is purified by recrystallization; it dissolves in boiling water; it may be sublimed, and condenses in long needles, like benzoic acid; it possesses the usual acid properties; its salts are generally soluble, and resemble closely the benzoates.

By the action of chlorine on salicide of hydrogen, *Chloride of Salicyle* is formed, Syl.Cl.; it crystallizes in rhomboidal tables, which melt and sublime undecomposed; bromine and iodine give similar compounds; with nitric acid it produces *Nitrosalicylic Acid*, Syl.N.O_4, which crystallizes in long prisms, and unites with bases forming salts.

The connexion of salicyl with benzyl is very remarkable; they contain the same hydrogen and carbon, $C_{14}H_5$, but it is combined in salicyl with 4, and in benzyl with but 2 atoms of oxygen. By the action of ammonia on the chloride of salicyl and on the oil, this relation is more clearly shown, for the oxygen in the radical may be brought to the composition of benzyl. Thus the *Chlorosalicamide* is $C_{42}H_{15}Cl_3 . O_6N_2$, or, properly, $3(C_{14}H_5O_2 . \frac{2}{3}N.)Cl.$; that is, $(Bz.\frac{2}{3}N.)Cl$. By the direct action of ammonia on the salicide of hydrogen, the corresponding $(C_{14}H_5O_2 . \frac{2}{3}N.)+H.$ may be formed. To this new radical, which is evidently *Nitruret of Benzyl*, the name *Azosalicyl* might be given (see p. 572).

Essential Oil of Mustard.

The oil obtained by distilling the seeds of the sinapis nigra with water is remarkable for an unusually complex constitution, as it contains five elements; its formula being $C_{32}H_{20}N_4 . S_5O_5$. When pure, it is colourless; it boils at 289°; its specific gravity is 1·015; that of its vapour is 3370; when acted on by nitric acid, it yields sulphuric acid and an organic product; with caustic potash it forms sulphuret and sulphocyanuret of potassium, and organic products which have not been examined. With ammonia it forms a substance in large white crystals, the formula of which is $C_{32}H_{20}N_4 . S_5O_5+4N H_3$. Our knowledge of the chemical nature of this oil is yet imperfect. It has been only established that it does not exist in the seeds, being, like oil of bitter almonds, formed at the moment of distillation.

The seeds of mustard contain two crystalline substances. Of these, *Sulphosinapisine* is obtained by a process similar to that used for preparing amygdaline. It is, when pure, white; soluble in alcohol and water; it contains the same five elements as the oil, which is probably formed from it by the action of the emulsin of the seed, as is the case with amygdaline. The principle of the mustard seed to which it appears to owe most of its pungency has been termed *Sinapisine;* its preparation is complex; it does not contain any sulphur, and hence can act but indirectly in the formation of the essential oil. Fremy considers the essential oil to be formed by the action of the albumen of the seed on a peculiar acid body, which he terms *Myronic Acid;* but this has not been analyzed, and we do not know its relations to sinapisine, with which it may possibly be identical. The formula given above for the oil is that of Dumas; Löwig has since analyzed it, and denies that it contains oxygen, assigning to it the formula $N.C_8 . H_5S_2$. Accurate researches on the constitution of these bodies are very much to be desired.

2D CLASS.—*Oils pre-existing in the Plant. Properties not Acid*

These oils are very numerous, and so similar in properties that a special description is quite unnecessary for each. They are characterized by not dissolving in solution of potash, by being lighter than water, and by a less energetic action on the animal system than the oils of the first class. They combine with muriatic acid to form heavy oily substances, in some cases crystalline. When put in contact with iodine, they frequently combine with it so energetically as to produce a feeble explosion. By chlorine, hydrogen is removed, and an oily liquid, heavier than water, is produced. The oil, as yielded by the plant, consists of two substances, one solid (*Stearopten*), the other liquid (*Elaopten*); the former generally crystallizes when the oil is long kept. I prefer to term the liquid simply the *oil*, and the solid portion the *camphor* of the plant. We sometimes observe these oils forming the camphor artificially, by contact with water.

These oils may be very naturally divided into two groups, according as they contain oxygen or not. The following table includes all the important facts of the history of the oils (elaoptens) containing oxygen:

Plant yielding the oil.	Sp. gr. as Liquid.	Boiling Point.	Formula.	Sp. gr. of Vapour.
Cajeput	0·927	347°	$C_{10}H_9O$.	
Lavender	0·896	397°	$C_{15}H_{14}O_2$	
Rosemary	0·897	365°	$C_{45}H_{38}O_2$	
Pennyroyal	0·925	395°	$C_{10}H_8O$.	
Camphor-tree	0·910	. .	$C_{20}H_{16}O$.	
Valerian	. .	518°	$C_{20}H_{12}O$.	
Spearmint	0·914	. .	$C_{35}H_{28}O$.	
Marjoram	0·867	354°	$C_{50}H_{40}O$.	
Asarum	. .	. .	$C_{16}H_9O_2$	
Fennel	0·997	. .	$C_{20}H_{12}O_2$	
Anise	. .	. .	$C_{20}H_{12}O_2$	
Peppermint	0·902	. .	$C_{21}H_{20}O_2$	
Rue	0·837	446°	$C_{25}H_{25}O_3$	7690
Olibanum	0·866	323°	$C_{35}H_{28}O$.	
Cumin	0·860	418°	$C_{20}H_{12}O_2$	5094

From the recent experiments of Gerhardt and Cahours, it appears that, by the action of fused hydrate of potash, most essential oils containing oxygen may be separated into an acid, and an oil destitute of oxygen. Some of the results obtained by those chemists are of great interest; thus, from the oil of valerian, $C_{20}H_{12}O$., valerianic acid is obtained, and an oil which absorbs oxygen with great rapidity and generates common camphor. The oil of chamomile also yields valerianic acid.

The oil of cumin (cuminum cyminum), of which the characters have been given in the table, yields, when treated with hydrate of potash, a peculiar acid, *Cumenic Acid,* whose formula is $C_{20}H_{11}O_3+Aq.$; it is perfectly white, crystallizes in fine prismatic tables, tastes sour, fuses at 197°, and may be distilled unchanged. If cumenate of barytes be distilled at a dull red heat, a colourless liquid oil is obtained, which boils at 292°; it is termed *Cymen;* its formula is $C_{18}H_{12}$, being isomeric with mesitylene; with sulphuric acid cymen unites, forming *Cymensulphuric Acid,* $C_{18}H_{12} . S_2O_6$, which forms well-characterized soluble salts. By the action of chlorine and of bromine on the oil of cumin, heavy oily compounds are obtained, whose formulæ are $C_{20}H_{11} . O_2Cl.$, and $C_{20}H_{11} . O_2Br.$

It is evident that in these compounds a radical (*Cumyl*), $C_{20}H_{11}O_2$, exactly analogous to benzyl, may be assumed, and the cymen has the place of benzin. The carbohydrogen of the oil of cumin is termed by Cahours *Cumen;* its formula is $C_{20}H_{14}$; its specific gravity 0·860; it boils at 330°; it may be prepared artificially also from common camphor; with sulphuric acid it forms *Cumensulphuric Acid,* which resembles completely the other acids of that class.

The stearoptens, or camphors containing oxygen, will be described by-and-by.

The following table contains a similar view of the most important oils not containing oxygen:

Plants yielding the Oil.	Sp. gr. as liquid.	Boiling Point.	Formula	Sp. gr. as Vapour.	Circular Polarizing Power
Citron	0·847	343°	All these oils have the same composition, expressed by the formula C_5H_4.	All these oils give vapours with the specific gravity =4766.	+80° 9′, right
Copaiva	0·878	473°			+34° 3′, left.
Parsley	. . .	410°			. . . . . .
Juniper	0·839	311°			—3° 5′, left.
Savine	. . .	315°			. . . . . .
Cubebs	0·929	. . .			—40° 1′, left.
Black Pepper . . .	. .	. . .			. . . . . .
Bergamotte	. .	. . .			+29° 3′, right.
Turpentine	0·864	315°			—43° 3′, left.

Although these oils have all the same per cent. composition, they differ in the formula of their atom, that of turpentine being $C_{20}H_{16}$, that of cubebs, $C_{15}H_{12}$, and all the others being $C_{10}H_8$. Although, even as given in the table, they constitute a remarkable group of isomeric bodies, yet each one is capable of changing its molecular condition in various ways, and thus generating other bodies, still more closely isomeric, as they differ only in their action on polarized light. Of these changes I shall describe only those of oil of turpentine, which will serve as an example.

By contact with oil of vitriol, oil of turpentine changes into another liquid, which has the same specific gravity both in the state of liquid and of vapour, the same boiling point, and the same atomic weight, but is totally without action on polarized light. This new liquid is called *Terebene*. If the oil of turpentine be acted on by muriatic acid gas, it combines therewith, forming a dense liquid, which is muriate of terebene, and which has no action on light; but another portion of the turpentine unites with the muriatic acid unchanged, and forms a solid, which crystallizes in fine white prisms, and, from its remarkable odour, is called *artificial Camphor*. In this solid the oil of turpentine preserves all its action upon light, and, for convenience, it may obtain the name *Camphene*, and the solid is then *Muriate of Camphene*. Now if this solid be distilled with lime, the muriatic acid is removed and an oil obtained, which differs from camphene only in having no action on light, while it differs from terebene in forming with muriatic acid a solid product. This oil is termed *Camphilene*, and the *Muriate of Camphilene* is distinguished from the muriate of camphene in being quite destitute of rotatory power. From none of these products can the true oil of turpentine, or camphene, be regenerated. There are thus three forms of oil of turpentine, of which two give solid compounds, and the third a liquid, with muriatic acid; two are without action on light, but the camphene rotates powerfully to the left: with chlorine they all give heavy liquids, all of which have the formula $C_{20}H_{12}Cl_4$, but are distinguished from each other by their action upon polarized light; the *Chlorcamphene* presenting the anomalous character of a rotatory power to the right.

When oil of turpentine is mixed with nitric acid and gently heated, a thick and heavy oily substance is produced, apparently by their direct union, and may be separated by the addition of cold water. If, however, the materials be left to themselves, after some time, violent, almost explosive action sets in, copious red fumes are given off, and a resinous material formed, which, by boiling with more nitric acid, dissolves, and the solution, on cooling, yields crystals of *Turpentinic Acid*. Its composition was found by Bromeis to be $C_{14}H_6O_7 + Aq$. The exact theory of its formation has not been as yet ascertained.

The other oils of this class are capable of similar metamorphoses, which need not be specially detailed.

The type C_5H_4 exists probably in all essential oils, for it will be seen, by reference to the former table of oils containing oxygen, that their formulæ consist in multiples of C_5H_4, combined with oxygen, or with the elements of water.

B. *Of the Camphors or Stearoptens of the Oils.*

The most remarkable substance of this class is the common camphor,

which is extracted from the wood of the laurus and dryabalanops camphora by distillation with water. In the plant it is mixed with the camphor-oil ($C_{23}H_{16}O.$), from the gradual oxidation of which it appears to be produced.

Camphor forms a white semitransparent mass, crystallized in irregular octohedrons. It is very tough and difficult to powder; its specific gravity is 0·986; its taste is bitter; its odour is well known; it melts at 347°, and boils at 390°, subliming unaltered; it is sparingly soluble in water, but easily so in alcohol and ether; its formula is $C_{20}H_{16}O_2$. The specific gravity of its vapour is 5317, which might be considered as formed by one volume of vapour of camphene and half a volume of oxygen (4776+551·3). Hence camphor and camphor-oil may be looked upon as oxides of an oil of the turpentine family.

When camphor is heated with lime, water, and an oil, *Camphron* ($C_{30}H_{22}O.$), are produced. With muriatic acid it unites, forming a colourless liquid, whose formula is $C_{20}H_{17} . O_2Cl$. By boiling with strong nitric acid, it is completely converted into *Camphoric Acid.*

This acid crystallizes in small rhomboidal tables, which taste sour and bitter; it melts at 145°, gives off water, and leaves the anhydrous acid, which melts at 423°, and distils over at 518° without alteration. The formula of the anhydrous acid is $C_{10}H_7O_3$; the crystals contain an atom of water. The salts of camphoric acid are not important, and appear to differ in properties according as the dry or hydrated acid was employed to form them. The *Camphorate of Ether* is a dense liquid, which, with camphoric acid, forms the *Camphovinic Acid,* a thick, heavy liquid, which is decomposed by heat, and forms unimportant salts.

When camphor is distilled with glacial phosphoric acid, water is formed, and a volatile oil passes over, having the formula $C_{20}H_{14}$, and identical in every respect with the *Cymen* obtained from oil of cumin, as described in p. 575.

When camphor in vapour is passed over hydrate of potash, heated to about 700°, an acid is formed, which has the formula $C_{20}H_{17}O_3+Aq$. This *Camphoric Acid* fuses at 176°, and boils at 482°; it may be distilled unchanged. It is insoluble in water, but dissolves abundantly in alcohol and ether, and crystallizes from these solutions on cooling. When it is heated with phosphoric acid, a volatile oil is produced, *Campholën,* having the formula $C_{18}H_{16}$. When campholeate of lime is distilled, another oily fluid is formed, whose formula is $C_{19}H_{17}O$.

Of the camphors of the other volatile oils, only a few require any detailed notice. The characters of most of them are given in the following table:

Plant giving the Camphor.	Sp. Gr. as Liquid.	Melting Point.	Boiling Point.	Sp. Gr. of Vapour.	Formula.
Rose (Otto)	. . .	77°	550°	. . .	C.H.
Parsley	. . .	70°	552°	. . .	$C_{12}H_7O_4$
Iris Florentina	. . .	. . .	. . .	. . .	$C_4H_4O.$
Elicampane	. . .	108°	. . .	. . .	$C_7H_5O.$
Asarum	. . .	104°	530°	. . .	$C_{16}H_{11}O_4$
Fennel	1·014	68°	428°	. . .	$C_{20}H_{12}O_2$
Anise	. . .	64°	430°	5680	$C_{20}H_{12}O_2$
Peppermint	. . .	91°	406°	5455	$C_{21}H_{20}O_2$
Cubebs	. . .	. . .	. . .	. . .	$C_{16}H_{14}O.$
Turpentine	1·057	302°	311°	. . .	$C_{20}H_{20}O_4$

On comparing these formulæ with those of the corresponding oils (p. 575), it is seen that the camphors arise from various causes; in some cases they are isomeric with the oils, in others oxides of them, and in others hydrates; thus the camphor of turpentine may be formed at will, by agitating the oil with water, and then exposing it to cold; the hydrate crystallizes out in colourless prisms, sometimes of great size.

The peppermint-camphor has been found to yield, by the action of re-agents, a series of compounds. Thus, by the action of glacial phosphoric acid or of oil of vitriol, a light oil was obtained, having the formula $C_{21}H_{18}$, which is termed *Menthen*. By the action of chlorine, a thick, heavy liquid is produced, $C_{21}H_{14} . Cl_6O_2$. By nitric acid, menthen yields a heavy oily liquid, $C_{21}H_{18}O_9$, which possesses acid properties; and with chlorine, menthen yields a sirupy yellow liquid, having the formula $C_{21}H_{13}Cl_5$.

The anise-camphor yields with bromine a crystalline substance, $C_{20}H_9 . Br_3O_2$, and with sulphuric acid an oily substance, *Anisoïne*, isomeric with itself. By nitric acid it is converted into a body which crystallizes in long needles, *Anisic Acid*, $C_{16}H_6O_5 + Aq.$, which forms salts with metallic oxides, and gives by farther action the *Nitranisic Acid*, $C_{16}H_5 . N.O_3 + Aq.$, and *Nitranisid*, $C_{20}H_{10} . N_2O_{10}$.

C. *Of the Resins.*

The bodies of this class approach closely to the camphors in composition and properties, but are distinguished by not being volatile without decomposition, and being generally capable of acting as acids. The most important will be first specially noticed, and the properties and formulæ of the remaining expressed in a table.

Resins of Turpentine.—The ordinary white resin coexists, in the different species of pine, with oil of turpentine, and is obtained by making incisions through the bark, when the thick, tenacious turpentine flows out. This, when distilled with water, gives off the oil, while the resin remains, and is called *Colophony*. It is a mixture of two resins, which, though having the same composition, differ in properties, and are termed the pinic and sylvic acids.

The *Pinic Acid* is obtained by digesting colophony reduced to fine powder, in cold spirit of sp. gr. 0·865, which does not dissolve sylvic acid. The solution is to be mixed with a spirituous solution of acetate of copper as long as a precipitate forms. This *Pinate of Copper* is to be dissolved in strong boiling spirit, decomposed by a little muriatic acid, and then mixed with water; the pinic acid precipitates as a resinous powder, which may be dried at a moderate heat.

When quite pure, pinic acid is colourless; it melts at 257°, but becomes soft at 149°: its solution in alcohol reacts acid. It expels carbonic acid from bases; its alkaline salts are soluble; its earthy and metallic salts insoluble in water, but many of them soluble in spirit; its formula is $C_{40}H_{30}O_4$.

When a solution of pinic acid in alcohol is long exposed to the air, it absorbs oxygen and forms *Oxypinic Acid*, the formula of which is $C_{40}H_{30}O_8$; it is a stronger acid than the pinic. When heated with lime, pinic acid is decomposed, and three different volatile oils obtained, which need not be specially noticed.

The *Sylvic Acid* remains when the pinic acid is dissolved by weak alcohol. As it is not pure, the residue is to be dissolved in two parts of

boiling spirit of 0·865 ; on cooling, the sylvic acid separates. By a second solution, all the traces of pinic acid may be removed. The pure sylvic acid crystallizes from its alcoholic solution in colourless rhombic prisms ; it melts at 212° ; it is easily soluble in strong alcohol and in ether, but insoluble in water ; its formula is $C_{40}H_{30}O_4$. Its salts are exactly similar to those of pinic acid.

When either pinic or sylvic acids are kept melted for some time, they become brown, and change into a resin very sparingly soluble in alcohol, and possessed of stronger acid properties than either ; it is termed *Colophonic Acid;* it exists in small quantity in common resin.

The resin of the spruce fir has been found by Johnstone to be a mixture of two resins, which are separated by means of alcohol. The more soluble, or A resin, has the formula $C_{40}H_{31}O_6$; the less soluble, or B resin, that of $C_{40}H_{39}O_5$; they both possess acid characters.

For the manufacture of tar and pitch, the pine wood containing turpentine is exposed to a kind of destructive distillation, in kilns hollowed out in the ground. Although a large quantity of the resin flows out undecomposed (as colopholic acid), yet the important components of the tar are bodies belonging to a different series, which will be described hereafter.

A great variety of resins, of important use in medicine and in the arts, exude from trees, either pure, or mixed with oils, or with gums (*Gum Resins*), sometimes with benzoic or cinnamic acids, constituting *Balsams.* Frequently there are many kinds of resins mixed together, but they all possess the characters of fusibility, insolubility in water, and of being dissolved by alcohol, ether, essential oils, and alkaline solutions. Their composition is given in the following table :

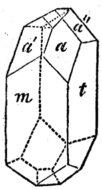
Anime Resin	$C_{40}H_{33}O$.	B. Sandarach	$C_{40}H_{31}O_6$
Elemi Resin		A. Euphorbium . . .	
Fossil Copal	$C_{40}H_{32}O$.	Asphaltene	$C_{40}H_{32}O_6$
B. Mastic Resin . . .	$C_{49}H_{31}O_2$	A. Olibanum	
Antiar Resin	$C_{40}H_{30}O_2$	Labdanum	$C_{48}H_{33}O_7$
B. Copal Resin . . .	$C_{40}H_{31}O_3$	Pasto Resin	$C_{40}H_{32}O_8$
Birch Resin	$C_{40}H_{35}O_3$	Sagapenum	$C_{40}H_{29}O_9$
A. Mastic Resin . . .	$C_{40}H_{31}O_4$	Scammony	$C_{40}H_{33}O_{20}$
Copaiva Resin . . .		Jalap Resin	$C_{40}H_{34}O_{20}$
A. Elemi Resin . . .	$C_{40}H_{32}O_4$	Galbanum	$C_{40}H_{27}O_7$
B. Olibanum Resin . .		Dragon's Blood . . .	$C_{40}H_{21}O_8$
C. Sandarach	$C_{40}H_{30}O_6$	Gamboge	$C_{40}H_{23}O_8$
Ammoniac Resin . . .	$C_{40}H_{25}O_9$	A. Assafœtida	$C_{40}H_{26}O_{19}$
B. Assafœtida	$C_{40}H_{26}O_9$	Acaroid Resin	$C_{40}H_{20}O_{12}$
Guiacum	$C_{45}H_{23}O_{10}$	Opoponax	$C_{40}H_{25}O_{14}$
Bdellium Resin . . .	$C_{40}H_{31}O_5$	B. Benzoin Resin . . .	$C_{40}H_{22}O_9$
A. Sandarach		A. Benzoin Resin . . .	$C_{40}H_{26}O_7$

In all this series of resins, it is evident that the carbon remains unaltered, and Johnstone has shown that they may all be considered as derived from oils having the turpentine constitution $=C_{40}H_{32}$.

A substance which is connected with the preceding in many ways is *Amber.* This body is found in rounded pieces, mixed with or attached to fragments of decomposing wood, in the lignite beds of the north of Europe. It is also found, cast on shore by the waves, along the coast of the Baltic. It is yellow, transparent, and often contains imbedded in it insects and parts of plants, so as to prove it to have been perfectly liquid when first formed. It is, in fact, the turpentine of unknown trees, belonging to a former geological epoch ; its specific gravity is 1·067 ;

when heated it melts, and is then totally decomposed; its relations to electricity have been fully noticed, p. 108. Amber is found to be a mixture of two resins, which are soluble in alcohol and ether, a bitumen insoluble in those liquids, a volatile oil, and a peculiar acid, the *Succinic Acid.* It is used very extensively in the arts as a material for varnishes, but to chemists its principal interest is its electrical properties, and as a source of its acid.

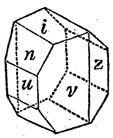
Succinic Acid is obtained by the destructive distillation of amber; it partly sublimes into the neck of the retort, in discoloured crystals, and partly dissolves in the water which comes over; by solution in nitric acid it may be freed from the resinous colouring matters. It may also be obtained from the amber by digestion with alcohol or solution of potash; it hence pre-exists in the amber, and is not produced by the heat. It is found in small quantity also in colophony, and is abundantly produced by the action of nitric acid on the fatty acids, as the stearic or margaric.



Succinic acid crystallizes, from its solution in water, in colourless right rhombic prisms, as *m, t, a* in the figure, which have the formula $C_4H_2O_3+Aq.$; when heated to 350° it melts, abandoning half its water, and at 450° sublimes in an anhydrous state; its solution in water is markedly acid; when heated with lime, a volatile liquid is produced, *Succinone,* the exact formula of which is not established.

The salts of succinic acid are mostly soluble and crystallizable.

The *Succinate of Soda,* prepared by neutralizing the acid by carbonate of soda, crystallizes in doubly oblique rhombic prisms, of which *i, u, v* are primary, and *z, n* secondary faces in the figure; it is permanent in the air, and very soluble in water. The *Succinate of Ammonia,* which is much used in mineral analysis for the separation of iron from manganese, crystallizes in nearly the same form as the soda-salt figured above. The succinates of barytes, lime, and lead are white powders, insoluble in water. The *Succinate of Manganese* forms rose-red, four-sided prismatic crystals, permanent in the air, and soluble in ten parts of cold water. The *Succinate of the Peroxide of Iron* is precipitated when an alkaline succinate is added to any salt of iron not containing an excess of acid; it forms a pale brownish-red powder, insoluble in cold water, but decomposed by boiling water, which dissolves out the acid with a small quantity of the iron; it dissolves readily in acid liquors.



The *Bisuccinate of Ammonia* gives off water when heated, and a white crystalline solid sublimes, which is termed *Succinamid.* Its formula is $C_8H_5 . O_4N$.

The rare mineral, *Mellite* (see p. 498), is only found accompanying amber in the deposites of lignite.

Caoutchouc. Indian Rubber.—This substance, now so much used in the laboratory for connecting pieces of apparatus, and so extensively employed in the arts, possesses much similarity to the resins. It dissolves but imperfectly even in ether, its proper solvent being the volatile oils, into which it is converted by distillation. One of these is the lightest liquid known, its specific gravity being but 0.654; it boils at 92°; it has been termed *Faradyn.* Another, known as *Caoutchene,* has a specific

gravity of 0.842; it boils at 340°. The composition of these liquids, or of caoutchouc itself, is not well known, as they have not been, as yet, obtained absolutely pure; but, so far as I can judge, they appear all to have the same composition as oil of turpentine.

CHAPTER XXIII.

OF THE SAPONIFIABLE FATS AND OILS.

THE substances of this class are found both in the animal and vegetable kingdoms very extensively distributed. In animals, the various fats are deposited in the cavities of the cellular tissue, but often also diffused through the mass of the glandular organs. In plants, the oils or fats are generally found in the investing membranes of the seed, or in the cellular texture of the fruit. The leaves or roots seldom contain any fatty matter. The fats and oils, as they exist in nature, are mixtures of a few simple fatty and oily bodies in variable proportions, their degree of consistence depending on the relative preponderance of the solid or liquid constituent. The greater number of fats consist of two simple fats, *Stearine* and *Margarine*, and a simple oil, *Oleïn;* but these three bodies, which may be considered as the bases of all fats and oils, are accompanied generally by smaller quantities of solid or liquid fats, which are often peculiar to a particular animal or plant. These fatty bodies are all *fixed;* that is, they cannot be distilled without decomposition; but they are totally converted by heat into volatile bodies, undergoing, in some cases, singular metamorphoses, which will be described in the history of the individual fats.

Exposed to the air, the fatty bodies gradually absorb oxygen, and evolve carbonic acid; they at the same time obtain an acid reaction, and a smell well known as *rancid*. Most of this change appears to result from minute quantities of azotized organic tissues, which remain interspersed through the fats. A great number of oils, however, absorb oxygen very rapidly, and, evolving carbonic acid, change into a soft resinous body; they are hence termed *Drying Oils*, and are used so in painting. This drying quality is increased by combining the oil with a small quantity of a base, as oxide of lead.

The most important fact in the history of the fixed oils and fats is, that, by the action of alkalies, they are converted into *soaps;* whence the name of *saponifiable* given to the class. By means of the alkali, the fat or oil is decomposed into an acid, which combines with the base, forming a true salt, which is the *Soap*, and a substance soluble in water, of a sweet taste, which is the same, no matter what kind of fat had been employed. This substance, the *sweet principle of the oils*, or *Glycerine*, is united in each fat with a different acid, and hence, as the fats are best described as salts of glycerine, I shall first notice the composition and properties of the base itself.

Of Glycerine.—$C_6H_7O_5+Aq$. Eq. 1157·4 or 92·3. To obtain glycerine, any fatty matter is to be saponified by a caustic alkali. The solution being decomposed by tartaric acid, which precipitates the fatty

acid, is to be evaporated, and the glycerine dissolved out by strong alcohol. It may also be obtained by saponifying the fat by oxide of lead, and treating the watery solution with sulphuretted hydrogen to precipitate some oxide of lead, which dissolves; the glycerine may then be obtained by evaporation.

Glycerine cannot be obtained solid. When brought to its greatest degree of consistence by evaporation in vacuo over sulphuric acid, it is a colourless sirup, sp. gr. $=1{\cdot}26$; it dissolves in water and alcohol, but is insoluble in ether; it is decomposed by heat. With nitric acid it produces oxalic and formic acids. Boiled with solutions of copper, it precipitates metallic copper. With chlorine it forms a white flocculent solid, having the formula $C_{12}H_{11} . O_{10}Cl_3$, and with bromine it gives a dense oily liquid, whose formula is $C_{12}H_{11} . O_{10}Br_3$.

When glycerine is mixed with oil of vitriol, they unite without blackening, and form an acid compound, *Sulphoglyceric Acid*, the formula of which is $C_6H_7O_5 . 2S.O_3 . H.O$. With bases this acid forms soluble salts, having considerable analogy to the sulphovinates. The *Sulphoglycerate of Lime* crystallizes in long delicate needles, whose formula is $C_6H_7O_5 . S.O_3+S.O_3 . Ca.O$. The compounds of glycerine with the fatty acids constitute the various kinds of fats and oils.

Of Stearine and Stearic Acid.

Stearine is the essential constituent of all solid fats, and preponderates in proportion to their consistence. It is best obtained from mutton-suet, either by washing it with ether, as long as anything is dissolved, or by mixing up melted suet with six times its volume of ether, and subjecting the mass, when cold, to strong pressure. In both cases the stearine remains behind; it is generally crystalline like spermaceti, not at all greasy between the fingers, and is easily powdered; it melts at 143°; it is insoluble in water and in cold ether; it dissolves in boiling alcohol or ether, and crystallizes out as it cools. The formula of stearine is $C_{142}H_{141}O_{17}$, consisting of

$$\left.\begin{array}{ll}\text{1 atom of glycerine,} & =C_6H_7O_5,\\ \text{2 atoms of stearic acid,} & =C_{136}H_{132}O_{10},\\ \text{2 atoms of water,} & =H_2O_2,\end{array}\right\} =C_{142}H_{141}O_{17}.$$

By the action of strong bases or of strong acids, it is separated into these constituents. A similar decomposition is effected by heat.

Stearic Acid is obtained pure by saponifying stearine by potash, and decomposing the solution by means of warm dilute muriatic acid. The stearic acid which precipitates is to be washed with water and dissolved in boiling alcohol, whence the pure acid crystallizes, on cooling, in brilliant white plates.

When mutton-suet is directly saponified, very troublesome operations are necessary to free the stearic acid from the other fatty acids which accompany it.

Pure stearic acid is tasteless and inodorous. It does not melt below 158°; the melted acid forms a crystalline mass on cooling; it is apparently volatile, and may be distilled unaltered in close vessels; it is insoluble in water, but dissolves in hot alcohol; the solution reddens litmus; its composition, when crystallized, is $C_{68}H_{66}O_5+2$ Aq. When heated in contact with lime, carbonic acid is formed, and a volatile liquid, *Stearon,* whose formula is $C_{66}H_{66}O$.

Stearic acid is but feeble in its action: it expels the carbonic acid from the alkalies only when the solution is boiling. It is bibasic, forming two classes of salts, the *Bistearates*, which contain one atom of water and one of fixed base, and the *Neutral Stearates*, which contain two atoms of fixed base. The alkaline stearates are the only salts soluble in water; they dissolve also in alcohol. If neutral stearate of potash be mixed with a large quantity of boiling water, it is decomposed, one half of the potash becoming free, and the *Bistearate of Potash* precipitating in minute crystalline scales. A solution of soap precipitates all earthy and metallic salts, producing insoluble stearates.

The *Stearic Ether* is exceedingly remarkable, as it corresponds exactly to stearine in composition, the glycerine being replaced by ether. Thus its formula is

$$\left.\begin{array}{ll}\text{1 atom of ether,} & =C_4H_5O., \\ \text{2 atoms of stearic acid,} & =C_{136}H_{132}O_{10}, \\ \text{2 atoms of water,} & =H_2O_2,\end{array}\right\} C_{140}H_{139}O_{13}=\text{1 atom of stearic ether.}$$

Stearic acid is now very extensively used for making candles. The tallow is saponified by boiling with a thin paste of lime. The glycerine is washed out, and the soap being decomposed by muriatic acid, the oleic acid is removed from the stearic acid by violent pressure between folds of cloth. The pure stearic acid, when solidifying, assumes a crystalline structure, which would spoil the appearance of the candle, and this tendency is removed by the very improper addition of one part of arsenious acid to about 2000 of stearic acid.

Of Margarine and Margaric Acid.

Margarine exists along with stearine in most fats, but is most characteristic of human fat. It is prepared from the ethereal solution, which has left the stearine undissolved. This liquor is to be evaporated, and the residue dissolved in boiling alcohol, from which the margarine crystallizes as the solution cools; it melts at 118°. In all other properties it resembles stearine, but is much more soluble in ether and alcohol; it consists of $C_{74}H_{74}O_{12}$.

$$\left.\begin{array}{ll}\text{1 atom of glycerine,} & =C_6H_7O_5, \\ \text{2 atoms of margaric acid,} & =C_{68}H_{66}O_6, \\ \text{1 atom of water,} & =H.O.,\end{array}\right\} =C_{74}H_{74}O_{12}, \text{ 1 atom of margarine.}$$

By the action of bases it is separated into glycerine and margaric acid.

The preparation of *Margaric Acid* is precisely similar to that of the stearic acid, which it resembles very closely, being most different in its melting point, which is 140°. On solidifying, it crystallizes in white needles. When carefully heated, it volatilizes without alteration. The formula of margaric acid is $C_{34}H_{33}O_3+Aq$. If it be mixed with lime and distilled, carbonic acid is produced, which combines with the lime, and a volatile substance is obtained, which is termed *Margaron*. Its formula is $C_{33}H_{33}O$. It is a white solid, of a pearly lustre, which melts at 170°, and forms, on cooling, a crystalline mass like spermaceti. By repeated distillation with lime, all oxygen is removed as carbonic acid, and a volatile oily substance obtained, having the composition of olefiant gas.

The experiments of Redtenbacher have indicated a remarkable source of margaric acid in the distillation of stearic acid. The distilled product, though in appearance unchanged stearic acid, yet does not in reality

contain any trace of it, being a mixture of margaric acid, of margarone and of the volatile oily carbohydrogen. The reaction being that

4 atoms of hydrated stearic acid, $C_{272}H_{272}O_{28}$,	produce	6 atoms of margaric acid,	$C_{204}H_{204}O_{24}$,
		1 atom of water,	$H.O.$,
		1 " margarone,	$C_{33}H_{33}O.$,
		1 " carbonic acid,	$C\,O_2$,
		The oily carbohydrogen,	$C_{34}H_{34}$.

Redtenbacher doubts the real existence of stearone, as none of it is produced in this reaction.

The salts of margaric acid resemble perfectly the stearates in their properties, but the acid being monobasic, there is but one class of margarates. The pearly lustre of the crystalline scales of the margarate of potash gave occasion to the name of this acid, from the word *μαργαριτης, a pearl.*

If we compare the formulæ of the bodies now described, we find them capable of being expressed by a very simple theory: thus, indicating an hypothetic carbohydrogen, $C_{34}H_{33}$, by R., the stearic acid becomes R_2+O_5, and the margaric acid, $R.+O_3$, being related as hyposulphuric and sulphuric acids. Also, as Redtenbacher has remarked, all the results obtained might be accounted for by ascribing to margarone the formula $C_{34}H_{33}O.$, in which case it becomes $R.+O.$, and the volatile oil may be $R.+H.$ Farther researches are, however, wanted to give experimental evidence on these points.

Of Oleïn and Oleïc Acid.

Oleïn exists in small quantity in the various solid fats, but constitutes the great mass of the liquid fixed oils which are not *drying oils.* It holds dissolved, more or less, stearine and margarine, of which the greatest part may be separated by exposure to cold, when they crystallize. Olive oil contains a large quantity of margarine, and hence freezes very readily. The expressed oil of sweet almonds is the purest native oleïn; next to it is rape oil.

To obtain pure oleïn, almond oil is dissolved in hot ether, and the solution exposed to great cold; the traces of margarine crystallize out completely, and by evaporation the ether is removed. Oleïn remains liquid at 0° Fah. In constitution it resembles the solid fats, containing a peculiar acid, *Oleïc Acid,* combined with glycerine and water.

1 atom of glycerine,	$C_6H_7O_5$,	produce 1 atom oleïn,	$C_{94}H_{87}O_{15}$.
2 atoms of oleïc acid,	$C_{88}H_{78}O_8$,		
2 atoms of water,	H_2O_2,		

Oleïc Acid is obtained by saponifying oleïn with a strong solution of potash, then decomposing the oleate of potash by muriatic acid, washing the oil which separates, and drying it with chloride of calcium; when cooled below 20° F., it congeals as a mass of needly crystals. Its specific gravity at 60° is 0·898; it is tasteless and inodorous when pure; it is insoluble in water, but abundantly soluble in alcohol and ether; these solutions react strongly acid; its composition has been determined by Varrentrapp to be $C_{44}H_{39}O_4+Aq.$; its alkaline salts are soluble, and form soft masses, destitute of tendency to crystallize; they are still more soluble in alcohol. The earthy and metallic salts are white, plastery substances, insoluble in water. The *Oleate of Lead* is soluble in ether, by which it may be perfectly separated from the stearate or mar-

garate of lead. The *Oleïc Ether* was formed by Varrentrapp by passing muriatic acid gas into a solution of oleïc acid in alcohol. It is a colourless liquid, sparingly soluble in alcohol, lighter than water, but heavier than alcohol, from which it is deposited as it forms; its formula is $C_{44}H_{39}O_4 + Ae.O$.

When oleïc acid is distilled, a portion of it passes over unaltered, but the greater part is decomposed, and some charcoal remains in the retort. The distilled products are *Sebacic Acid* and a liquid carbohydrogen, isomeric with olefiant gas; sebacic acid is not produced by the distillation of any other fatty substance than oleïc acid, and hence may be considered as characteristic of it. The decomposition consists in that

$$\left.\begin{array}{c}\text{2 atoms of hydrated oleïc acid,}\\ C_{88}H_{80}O_{10},\end{array}\right\}\text{produce}\left\{\begin{array}{ll}\text{1 atom of sebacic acid,} & C_{10}H_9O_4,\\ \text{3 atoms of carbonic acid,} & C_3O_6,\\ \text{carbohydrogen,} & C_{71}H_{71},\\ \text{residual charcoal,} & C_4.\end{array}\right.$$

Sebacic Acid had been considered as a product of the destructive distillation of all fatty bodies; but it has been shown by Redtenbacher to arise only from oleïc acid; the distilled product is to be washed with boiling water, which dissolves the sebacic acid; on the addition of acetate of lead, a white precipitate is obtained, which, being decomposed by sulphuretted hydrogen, gives sulphuret of lead, while the pure sebacic acid dissolves, and may be obtained crystallized by the evaporation and cooling of its solution.

The crystallized sebacic acid closely resembles the benzoic acid in properties and appearance; its solution reddens litmus; its alkaline salts are very soluble; its lead, silver, and mercury salts are insoluble in water; from a strong solution of an alkaline *sebacate*, the acid is precipitated in voluminous crystalline flocks on the addition of a stronger acid. When completely pure, the sebacic acid is totally without odour, the strong smell of heated oil being due to the formation of a totally different substance, *Acroleon.* The dry sebacic acid has the formula $C_{10}H\ O_3$; when crystallized it becomes $C_{10}H_8O_3 + Aq$.

Of the Action of Nitric Acid on Stearic, Margaric, and Oleïc Acids.

By the gradual oxidation of those fatty acids, a series of bodies result, which have so much connexion with each other as to be most conveniently studied in relation to their origin.

A. If stearic acid be digested with two or three times its weight of common aquafortis at a moderate heat, a very lively action commences after some time, and copious red fumes are given off. When the mixture has ceased to froth up, and the action of the acid ceases, the only product forms a colourless layer on the surface of the acid liquor, and is found to be pure *Margaric Acid.* The change here is evidently a simple oxidation, as $R_2 + O_5$ and O. give $2(R. + O_3)$, as described in p. 584

If the fatty acid be acted on by successive quantities of the nitric acid until it disappears, the watery liquor deposites, on cooling, abundance of crystallized *Succinic Acid*, and the mother liquor of these crystals being evaporated to one half, forms, on cooling, a thick mass of crystals, which may be washed with cold water, and being purified by recrystallization, are found to be identical with the acid formed by the action of nitric acid on the peculiar woody tissue which exists in cork, *Suberine*, and which will be hereafter described. This acid is termed the *Suberic Acid;* it is white, inodorous, and of a feebly acid taste; easily soluble in alcohol and water; the crystals melt at 248°, and when heated more strongly, are decomposed in great part; it precipitates solution of acetate of lead; its alkaline salts are soluble and crystallizable; when crystallized, the formula of the acid is $C_8H_6O_3 +$ Aq. The *Suberic Ether* was prepared as described above for the oleïc ether; it is liquid, and its formula is $C_8H_6O_3 + Ae.O$. By the distillation of the suberate of lime, a volatile liquid, *Suberone*, is obtained, whose formula is C_7H_6O.

The artificial formation of the succinic and suberic acids in this way is exceedingly curious; but Bromeis and Laurent, to whom the observation is due, have not been able to trace the precise reaction in which they originate.

B. The action of nitric acid on oleïc acid is much more violent than on the stearic acid. Among the products of the reaction are found the succinic and suberic acids, but in addition, four other acid bodies, of which, however, a very slight notice will suffice.

The *Pimelic Acid* forms white crystalline grains, which melt at 273°, and sublime easily in brilliant needles; its alkaline salts are soluble, but its earthy and metallic salts insoluble in water; the formula of the acid is $C_7H_6O_3+Aq$.

Adipic Acid resembles closely the former; it dissolves in water, alcohol, and ether; melts at 223°; it sublimes in very beautiful crystals; its formula is $C_{14}H_9O_7+2$ Aq., it being a bibasic acid.

The *Lipic* and *Azoleic* acids are still less important, and our knowledge of their constitution very imperfect. All these bodies are obtained from the mother liquors, from which the succinic and suberic acids have crystallized.

The most important products of the action of nitric acid on oleïc acid, or on oleïn, are *Elaïdine* and the *Elaïdic Acid;* these bodies are of pharmaceutic interest, from their constituting the *Citrine Ointment*, or *Unguentum Nitratis Hydrargyri* of the Dublin and London pharmacopœias.

Elaïdine is prepared by the action of nitric acid, or, still better, of the red fumes of the nitrous acid on oleïn; the oil gradually becomes thick, and finally congeals into a butyraceous mass of a deep yellow colour. By digestion with warm alcohol, a deep orange-red oil is dissolved out, and the pure elaïdine is obtained perfectly white; it melts at 97°, is insoluble in water, and but sparingly so in alcohol; it dissolves readily in ether; with caustic alkalies, it saponifies completely, glycerine being set free. The whole action of the nitric acid in this reaction is exerted on the oleïc acid, and the elaïdine is a true fat, consisting of elaïdic acid united to glycerine.

Elaïdic acid may be prepared by saponifying elaïdine, and decomposing the alkaline elaïdate by a stronger acid, but it is obtained in a much purer form by passing nitrous acid fumes, generated by heating nitrate of lead (p. 276) into pure oleïc acid, prepared from oil of sweet almonds; after some time, the liquid becomes a nearly solid mass of crystalline plates, of a fine yellow colour; this mass is to be boiled in water to remove adhering nitric acid; then dissolved in boiling alcohol, and allowed to cool. The orange-red oil remains in solution, while the elaïdic acid crystallizes in large, brilliant, white rhombic tables. This body, when pure, fuses at 113°; it dissolves readily in alcohol and in ether; these solutions redden litmus; when boiled with a solution of carbonate of potash, carbonic acid is expelled, and elaïdate of potash formed; its earthy and metallic salts are insoluble in water. The crystallized elaïdic acid has the formula $C_{72}H_{66}O_5+2$ Aq.; it is a bibasic acid. The *Elaïdate of Silver* is hence $C_{72}H_{66}O_5+2Ag.O.$; and the *Elaïdic Ether*, which is a colourless fluid lighter than water, consists of $C_{72}H_{66}O_5+H.O.\ .\ Ae.O.$

The orange-red oil, which is formed simultaneously with the elaïdic acid, has not been, as yet, accurately examined, and hence we cannot explain by precise formulæ the mode in which these bodies are generated. It is this oil which gives to the *Citrine Ointment* its characteristic colour and smell; it is lighter than water, and dissolves in alkaline liquors, but does not form true soaps.

In the formation of citrine ointment, the conversion of the oleïn into elaïdine is effected by the nitrous acid which the solution of the mercurial salt always contains, it being formed by the deoxidation of the nitric acid, and there being no heat used to expel it. The subnitrate of mercury is then mechanically mixed with the elaïdine and with the yellow oil. Some of the mercurial salt is often decomposed, however, as metallic mercury may usually be detected interspersed through the ointment.

Both oleïc and elaïdic acids give origin, when heated with fused hydrate of potash, to a peculiar fatty acid, discovered by Varrentrapp; it is white, solid, and crystalline; melts at 144°, and has the formula $C_{32}H_{30}O_3+Aq$. There is formed, at the same time, a large quantity of acetic acid. Another point of connexion between the oleïc and elaïdic acids is, that by distillation both furnish sebacic acid.

The *Acroleon*, to which is due the exceedingly sharp and disagreeable smell of highly heated oil or fat, is generated by the decomposition of the glycerine, and in such exceedingly small quantity, that its isolation has not yet been successfully attempted. According to the observation of Brandes, it is a colourless oil, of sp. gr

0·578, which, when distilled with caustic soda, becomes inodorous, while the soda combines with a fatty acid ; no analytical investigation of it has been as yet made.

Action of Sulphuric Acid on Margarine and Oleïne.

When oleïn is mixed with oil of vitriol, the sulphuric acid combines with both the glycerine and the oleïc acid, forming sulphoglyceric and sulpholeïc acids. This last is soluble in water, but insoluble in dilute sulphuric acid ; and hence, by adding water gradually to the mixture of oil of vitriol and oleïne, it separates, floating as a thick sirup on the surface, while the sulphoglyceric acid and the excess of sulphuric acid dissolve. The sulpholeïc acid thus obtained forms, with lime and barytes, soluble salts, which are analogous to the sulphovinates ; when its solution in water is heated, it is decomposed, sulphuric acid becoming free, and the oleïc acid being converted into two acids, which have been named the *Metaoleïc* and the *Hydroleïc Acids*.

These acids are both liquid like oleïc acid ; they are principally distinguished, as to properties, by the sparing solubility of the former in alcohol, and are thus separated. The constitution of these bodies had been examined by Fremy at a time when the true constitution of the oleïc acid had not been established, and the formulæ he assigned to them are not now admissible. They are isomeric with each other; when distilled, they produce carbonic acid, and two volatile liquids, *Oleën* and *Elaën*, which are isomeric with olefiant gas. From the circumstances of the formation of these acids, the change must consist in the fixation of the elements of water, as no other body containing carbon is produced ; but, from his analysis, the anhydrous metaoleïc acid has evidently the same composition as the hydrated oleïc acid, and its formula is therefore $C_{44}H_{40}O_5$ when in combination, and $C_{44}H_{41}O_6$ when free. Its decomposition by heat consists in the separation of $3C.O_2$, and $C_{41}H_{41}$ remaining, which contains the elements of the two volatile oily liquids.

With margarine, oil of vitriol does not combine directly ; but if margarine and oleïn together, as they are in olive oil, be mixed with oil of vitriol, union occurs, and a sulphomargaric acid is produced, which, being treated similarly to the sulpholeïc acid, gives two other acids, the *Metamargaric* and *Hydromargaric*. These are soluble in alcohol, from which they crystallize by cold, so combined as to produce distinct salts, and to affect all the characters of an independent acid, called by Fremy the *Hydromargaritic*.

If the mixed solutions of sulphomargaric and sulpholeïc acids be left to decompose without heat, in place of being boiled, the metamargaric and metaoleïc acids separate and float on the top, but the hydromargaric and hydroleïc acids remain dissolved, and separate only by bringing the solution to boil. Each of the products thus obtained is to be dissolved in alcohol, and the modified margaric acids crystallize on cooling, while the modified oleïc acids remain dissolved. The metamargaric acid is polymeric with the margaric acid ; its formula is $C_{68}H_{66}O_6+2$ Aq., but the hydromargaric acid contains the elements of four atoms of water more, its formula being $C_{68}H_{70}O_{10}+2$ Aq.

Oleïn of the Drying Oils.

The oils which possess the property of rapidly absorbing oxygen and evolving carbonic acid, thereby being changed into a kind of transparent resinous varnish, consist of glycerine united to a liquid acid, quite distinct from the ordinary oleïc acid ; treated with nitric acid, it yields first a resinous substance, and then oxalic acid. The drying properties of these oils is known to be much increased by boiling on litharge, of which a quantity dissolves ; in this case, however, Liebig has shown that no saponification occurs ; the litharge serving only to combine with, and coagulate a quantity of vegetable mucus, which, being diffused through the oil, prevented its acting as rapidly on the air as it does when pure.

Of Cocoa-tallow and Cocoa-stearic Acid.

The albumen of the cocoa-nut contains a solid fat, which is extracted from it, and imported largely into these countries, to be used in the manufacture of candles. It is a mixture of ordinary oleïn with a stearine, which contains a peculiar acid. The oleïn and stearine are separated by pressure or by ether, or by solution in boiling alcohol, from which the stearine crystallizes on cooling, exactly as described for ordinary stearine.

The cocoa-stearine is white and crystalline ; its specific gravity is 0·925 ; insolu-

ble in water; it dissolves but sparingly in alcohol, except when boiling; it is more soluble in ether; it melts at 77°. The products of its decomposition by heat have not been well examined. With caustic alkalies it forms soaps, from which, by a stronger acid, the cocoa-stearic acid is separated.

This acid, purified by repeated crystallizations from alcohol, is brilliant white; it fuses at 95°, and cannot be distilled without total decomposition. Its formula was found by Bromeis to be $C_{27}H_{26}O_3+Aq.$; its alkaline salts are soluble, but the earthy and metallic salts are insoluble in water. By the process described for oleïc ether, the cocoa-stearic ether was prepared by Bromeis; it is a clear oil, lighter than water; its formula is $C_{27}H_{26}O_3+Ae.O.$

Palm Oil and Palmitic Acid.

This solid oil, which is now extensively employed in the manufacture of yellow soap, is prepared in Africa, by pressing and boiling the fruits of the cocos butyracea or of the avoira elais; it is of the consistence of butter, reddish-yellow colour, and an aromatic odour. When kept, it acquires a rancid smell, and becomes white; the colour results from a small quantity of a substance which may be decomposed, and the palm oil bleached by chlorine or any oxidizing agents. Besides ordinary oleïne, this oil contains a peculiar stearine, *Palmitine*, which has been accurately examined by Fremy and Stenhouse.

Pure *Palmitine* melts at 118°, and is crystalline. It is insoluble in water, very sparingly soluble even in boiling absolute alcohol, but abundantly soluble in ether. It is quite neutral; when saponified by potash, and the soap decomposed by an acid, palmitic acid is set free. The palm oil of commerce usually contains a large quantity of free palmitic acid, and hence is more easily saponified than any other fat; it also contains free glycerine, so that the palmitine would appear to undergo a spontaneous decomposition.

Palmitic Acid melts at 140°; it dissolves in hot alcohol, and crystallizes therefrom by cooling. Its formula in crystals is $C_{64}H_{62}O_6+2H.O.$; it is a bibasic acid; its silver salt is $C_{64}H_{62}O_6+2Ag.O.$ The *Palmitic Ether*, which may be prepared by heating palmitic acid with alcohol and oil of vitriol, is solid, and crystallizes in fine prisms, which melt at 70°, and have the formula $C_{64}H_{62}O_6+2Ae.O.$ By distillation, the palmitic acid is not altered; by the action of chlorine, hydrogen is removed from it, and an acid containing chlorine produced, the formula of which appears to be $C_{64}H_{54}\,.\,Cl_8O_6$.

The constitution of palmitine was found by Stenhouse to be expressed by the formula $C_{70}H_{66}O_8$, from which should follow, that the substance united with the palmitic acid is formed of $C_6H_4O_2$, and hence differs from common glycerine, $C_6H_7O_5$, in having lost the elements of three atoms of water. This would be a very important fact to reinvestigate.

Nutmeg Butter. Myristic Acid.

This substance is a mixture of an aromatic volatile oil, with three fats, of which two are easily soluble in alcohol, and are thus simply separated from the third, which has been termed by Playfair *Myristicine*. Of the fats soluble in alcohol, one is liquid and the other solid; but we do not know whether they are peculiar, as the analyses of Playfair have been confined to the third.

Pure myristicine is obtained by crystallization from its ethereal solution; it has a silky lustre, and melts at 88°. When saponified, it yields glycerine and *Myristic Acid*. This substance is snow-white and crystalline, easily soluble in hot alcohol, and then reddening litmus; it melts at 120°; its composition is expressed by the formula $C_{28}H_{27}O_3+Aq.$; its salts are very well characterized and crystallizable. The *Myristic Ether* is analogous in constitution to the stearic ether (583), consisting of

$$\left.\begin{array}{ll}\text{Two atoms of myristic acid,} & =C_{56}H_{54}O_6,\\ \text{One atom of ether,} & =C_4H_5O.,\\ \text{One atom of water,} & =H.O.,\end{array}\right\}\text{One atom of myristic ether, } C_{60}H_{60}O_8.$$

The myristicine was found by Playfair to have the formula $C_{118}H_{113}O_{15}$, consisting of

$$\left.\begin{array}{ll}\text{Four atoms of myristic acid,} & =C_{112}H_{108}O_{12},\\ \text{One atom of dry glycerine,} & =C_6H_4O_2,\\ \text{One atom of water,} & =H.O.,\end{array}\right\}C_{118}H_{113}O_{15}.$$

By distilling myristicine, much acroleon is generated, but no sebacic acid.

Ordinary Butter. Butyric, Caproïc, and Capric Acids.

Butter is a mixture of six different fats, viz., common stearine, margarine, and oleïne, with butyrine, caproïne, and caprine; by melting the butter, and keeping it for some days at a temperature of 68°, the stearine and margarine crystallize, while the others remain liquid. By means of alcohol, the oleïne is then separated from the other fats, which are more easily soluble in that menstruum; their farther purification depends on successive solutions in alcohol, but none of them can be considered as having been obtained completely pure.

Butyrine is a colourless oil, with the odour of heated butter. It solidifies at 32°; with alkalies, it gives a soap, and sets glycerine free. Its elementary composition is not known.

Caproïne and *Caprine* cannot be obtained sufficiently free from butyrine, or from each other, to be described.

When butter is saponified, and the soap decomposed by tartaric acid, stearic, margaric, and oleïc acids separate, while the other acids remain dissolved. On distilling this liquor, the butyric, capric, and caproïc acids pass over along with the water, and, being neutralized by barytes, the three barytic salts are separated by repeated crystallizations. Of these acids, the history of the *Butyric Acid* is most complete. It is a clear, oily liquid, of a penetrating, sour smell of rancid butter; tastes pungent and acid, and leaves a white mark on the tongue. Its specific gravity is 0·976; its boiling point is above 212°; it burns with a brilliant white flame, and is abundantly soluble in water, alcohol, and ether. Its formula is $C_7H_6O_3+Aq.$; when distilled with lime, it gives a neutral volatile liquid, *Butyrone*, whose formula is C_6H_6O. The *Caproïc Acid* agrees in properties closely with the butyric acid, but has a characteristic odour of sweat; its formula is $C_{12}H_9O_3=Aq.$ The *Capric Acid* crystallizes in fine needles, which melt at 66°, and have the formula $C_{18}H_{14}O_3+Aq.$

Of Fish Oils, Delphinine, and Delphinic Acid.

These oils are generally composed of ordinary margarine, stearine, and oleïne, but some, as whale oil and dolphin oil, contain a peculiar fat, *Delphinine*, which yields *Delphinic Acid.* From the fish oil the delphinine is extracted by cold alcohol, which dissolves it more readily than the other oils; it is liquid, of specific gravity 0·954; it is not acid, but becomes so by exposure to the air; it saponifies readily. From the soap, the delphinic acid is separated by tartaric acid, and may be obtained pure by distillation. It is a thin oil, of specific gravity 0·932; it boils above 212°, and distils unchanged; it has a peculiar aromatic smell; tastes acid, and reddens litmus strongly; it dissolves in twenty parts of water; its formula is $C_{10}H_9O_3+Aq.$, and when distilled with lime, it gives a volatile neutral liquid, *Delphinon*, C_9H_9O.

The delphinic acid has been found in the berries of the viburnum opulus, and its composition being the same, and its properties very closely resembling those of the valerianic acid, I think it very likely that a re-examination of it would demonstrate its identity with that remarkable vegetable acid.

Of Castor Oil and its Products.

The oil of the ricinus communis (castor oil) is, according to Lecanu and Bussy, a mixture of three fats, ricino-stearine, ricino-oleïne, and ricine, which are all easily soluble in alcohol. Like the fats of butter, they can be but imperfectly separated; but, when saponified, they yield acids, which can be more accurately examined: the soap, being decomposed by muriatic acid, yields an oil, from which, by cooling, the *Ricino-stearic Acid* crystallizes, and the remaining oil, when distilled, separates into the *Ricinic Acid,* which passes over, and the *Ricin-oleïc Acid,* which is not volatile.

Purified by recrystallization from alcohol, the ricino-stearic acid forms pearly scales, which are easily soluble in alcohol, redden litmus, and do not melt below 266°. The ricin-oleïc acid freezes a few degrees below 32°. The ricinic acid is solid and crystalline, melts at 71°, and distils unchanged at a temperature but little higher.

When castor oil is acted on by nitrous acid, it is converted into a solid substance, termed by Boudet *Palmine;* it is white, of a waxy appearance, and melts at 151°; it is easily soluble in alcohol and ether; with alkalies, it yields glycerine and *Palmic Acid.* We do not possess any knowledge of the elementary composition of these bodies.

The products of the complete oxidation of castor oil by nitric acid have been accurately examined by Mr. Tilly. The action is violent, and much nitrous acid fumes are given off. Besides suberic and lipinic acids, a peculiar fatty acid is formed, which is colourless, of an agreeable smell, and a sweet, stimulating taste; it boils at 300°, but cannot be distilled without being in great part decomposed. Its formula was found to be $C_{14}H_{13}O_3+Aq.$; he formed the ether of this acid in the way described for oleïc ether, and ascertained its formula to be $C_{14}H_{13}O_3+Ae.O$. This body is termed the *Perœnanthic Acid*, as it contains the same carbon and hydrogen as the œnanthic acid which exists in wine, as described in page 567, but combined with an atom more of oxygen.

Oil of Tiglium. Crotonine. Crotonic Acid.

The experiments that have been made on this oil have not given very satisfactory results: by saponification, it yields an acid which is exceedingly volatile; but whether the active properties of the oil reside in this crotonic acid is not established, nor have any analytical results been obtained as to its constitution.

Of the Manufacture of Soaps and Plasters.

Although the general principles of the constitution of soaps have been frequently alluded to in the description of individual fatty substances, and a detailed account of their manufacture would be out of place in the present work, yet it may not be uninteresting to notice briefly some circumstances of the processes employed, which could not be deduced from the mere theory of their nature, and yet are essential to practical success.

There are found in commerce three varieties of soap: 1st, *hard white soap*, which is made from tallow and caustic soda; 2d, *hard yellow soap*, which is made from soda with tallow, palm oil, and resin; 3d, *soft soap*, in which the alkali is potash, combined with whale or seal oil, and some tallow. The difference of consistence depends principally upon the alkali; as the fatty salts of soda unite with water to form true hydrates, which are completely solid, while the potash salts absorb water, and form a semitransparent gelatinous mass, such as is the ordinary soft soap.

For the preparation of the hard white soap, a solution of caustic soda is prepared, of specific gravity 1·050, by decomposing soda-ash by the proper quantity of lime; the soda-ley being brought to boil, the tallow is added in small portions at a time, until the free alkali has been all combined with fatty acids, and the ley will saponify no more. The liquor contains then free glycerine, and the fatty salts of soda, all dissolved together in the water; and as the soap scarcely crystallizes, a peculiar method is necessary to separate it from the solution. This is founded on the fact that soap is insoluble in a solution of common salt. If to a solution of soap in water, as much common salt be added as the water can dissolve, the soap is separated, and floats on the surface of the liquor completely deprived of water. But this is not the state in which the manufacturer wishes it to be. Hence the salt is added but gradually to the soap-ley, and the water then dividing itself between the salt and the soap, a point is obtained at which the soap is in its proper hydrated condition, and this being recognised by the appearance of the boil and the texture of the layer of soap, the latter is run into wooden boxes, where it congeals, and is then cut by a wire into the forms it has in commerce.

The hard white soap thus made generally contains from forty to fifty per cent. of water. When very hard it still retains above thirty, and may hold seventy per cent. without being very soft.

The formation of the *Yellow*, or *Resin Soap*, depends on the direct combination of an acid resin (colophony, p. 578) with soda. In this

case no glycerine is set free, as there is no proper saponification. A mere compound of resin and soda would be, however, too soft, and also act too powerfully on clothes; and hence there is always a quantity of fat added, generally tallow, and some palm oil, which brightens the colour, and masks the disagreeable odour of the resin. A good soap should contain two parts of fatty matter to one of resin.

The *Soft Soap* is manufactured by heating the oils in shallow pans, and gradually adding a strong solution of caustic potash, boiling and continually agitating the mass until the milkiness produced by the oil vanishes, the mass becomes transparent, and the froth subsides. As this soap cannot be separated from the liquor by the addition of common salt, which would decompose it, forming a soda-soap and chloride of potassium, the liquor is evaporated until the operator recognises that it has attained the proper strength, and it is then cooled as rapidly as possible. The glycerine of the oils exists, therefore, mixed through the substance of the soap. To give it greater consistence, some tallow is generally employed; and the stearate of potash crystallizing gradually, forms the white points which are seen in most specimens of soft soap.

Plasters are metallic soaps. Of these, the only one of pharmaceutic importance is the *Litharge Plaster*, prepared by boiling litharge, olive oil, and water together; oleate and margarate of lead are formed, and float upon the surface; when the mass has obtained the proper consistence, it is removed, and formed into rolls for use. The watery solution contains glycerine and a large quantity of oxide of lead dissolved. If litharge plaster be digested in ether, oleate of lead dissolves, and the margarate of lead is left behind.

Of Spermaceti, Ethal, and the derived Bodies.

Spermaceti exists in the cavities of the head of the physeter macrocephalus, and some allied species of whales, dissolved in the spermaceti oil, from which it separates by crystallization after the death of the animal. To obtain it pure, it is to be crystallized repeatedly from its alcoholic solution by cooling; it is a remarkably beautiful crystalline fat, melting at 120°, and volatilizing at 680° without change, if the air be excluded. By boiling with very strong alkaline solutions, it gradually saponifies, a margarate and an oleate being formed; but in place of glycerine, a peculiar base, which is termed *Ethal*, being set free. To obtain it pure, spermaceti is saponified by being fused with half its weight of potash; the resulting mass being digested with water and muriatic acid, the oily acids and the ethal separate from the liquor and float upon the surface. Being then mixed with lime, which combines with the oily acids, and boiled in absolute alcohol, the ethal dissolves, and crystallizes out on cooling.

It is a solid crystalline white substance, destitute of taste or smell; neutral to test paper; it melts at 119°, and volatilizes rapidly at 250°; it is insoluble in water; its formula is $C_{32}H_{34}O_2$, or $C_{32}H_{33}O.+Aq$. The spermaceti itself consists of

$$\left.\begin{array}{ll} \text{2 atoms of margaric acid,} & =C_{68}H_{66}O_6, \\ \text{1 atom of oleïc acid,} & =C_{41}H_{39}O_4, \\ \text{3 atoms of ethal,} & =C_{69}H_{102}O_6, \end{array}\right\} C_{208}H_{207}O_{16}, \text{ one equivalent of spermaceti.}$$

The ethal is remarkable for its analogy, in composition and properties to the bodies of the alcohol group; like them, it may be looked upon as

formed of water united to a carbohydrogen, isomeric with olefiant gas, and by distilling ethal with glacial phosphoric acid, this body is actually obtained, and has been termed *Cetene*. It is an oily liquid, colourless, soluble in alcohol and ether; it boils at 527°. From its reactions and the specific gravity of its vapour, 7846, it results that its formula is $C_{32}H_{32}$.

If ether be heated with perchloride of phosphorus, a heavy liquid is obtained, having the formula $C_{32}H_{33}Cl.$; and by fusing ethal with potassium, hydrogen is evolved, and a white solid substance formed, consisting of $C_{32}H_{33}O.+K.O.$, which, with water, gives hydrate of potash and ethal. With sulphuric acid ethal forms sulphoethalic acid, which resembles the sulphovinic acid, and has the formula $C_{32}H_{33}O..S.O_3+S.O_3.H.O.$ Farther, if the ethal be heated with potash, hydrogen gas is given off, and an acid formed, the formula of which is $C_{32}H_{31}O_3+Aq.$: it is termed the *Ethalic Acid.*

From this analogy of ethal to wine-alcohol, a compound radical, *Cetyl*, similar to ethyl, may be assumed to exist in these combinations, and its formula be written $C_{32}H_{33}$ or Ct. Ethal is then $Ct.O.+Aq.$ (See p. 566.)

Wax.—Ordinary beeswax is a mixture of two substances, which are separated by boiling alcohol. *Cerine* dissolves; it is quite white; its specific gravity is 0·969; it is less fusible than wax; it does not combine with bases; its formula is $C_{20}H_{20}O_2$. The substance insoluble in alcohol is *Myricine*, which melts at 95°; its formula is $C_{20}H_{20}O$. In yellow wax a colouring matter is present which has not been examined. When wax is bleached by nitric acid, oxygen is absorbed, and a peculiar substance formed, *Ceraic Acid*, which has the formula $C_{20}H_{20}O_3$. All these bodies are probably derived from oils, isomeric with otto of roses, which exist in the flowers of odoriferous plants.

When cerin is boiled with solution of potash, a soap is formed, and from this a peculiar waxy substance (*Ceraïne*) is obtained, as ethal is from spermaceti: its properties are but very little known; from an analysis by Ettling, its formula would appear to be $C_{18}H_{19}O_7$.

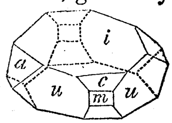
CHAPTER XXIV.

OF THE ORGANIC ACIDS WHICH PRE-EXIST IN PLANTS, AND DO NOT BELONG TO ANY ESTABLISHED SERIES.

Tartaric Acid.—$C_8H_4O_{10}+2\,Aq.$

THIS important acid exists in most kinds of fruit, occasionally free, but more usually combined with potash, forming cream of tartar, or as tartrate of lime. For the purposes of commerce, it is almost exclusively prepared from the bitartrate of potash. This salt exists abundantly in grape-juice, and being but very slightly soluble in spirituous liquors, it gradually separates as the alcoholic fermentation proceeds, and collects in irregularly crystallized layers on the insides of the casks in which the wine is made. It is purified, as will be elsewhere described.

When one part of carbonate of lime is added to a solution of four parts of bitartrate of potash, one half of the tartaric acid combines with the lime, carbonic acid being expelled with effervescence. Tartrate of lime precipitates as a white powder, and neutral tartrate of potash remains dissolved. By the addition of chloride of calcium to the liquor, this portion, also, of tartaric acid is thrown down, and chloride of potassium is formed. The whole quantity of tartrate of lime being then collected and washed, it is to be digested with a quantity of oil of vitriol, half the weight of the cream of tartar employed, and diluted with four parts of water; sulphate of lime is formed, and tartaric acid set free. The mixture, having been boiled for a short time, is to be strained, and the liquor evaporated gently to a pellicle; the tartaric acid then crystallizes on cooling.



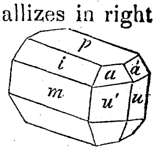
The tartaric acid forms colourless oblique rhombic prisms, generally tabular, as in the figure, where *i*, *u*, *u* are primary, and *a*, *c*, *m* secondary faces; it is permanent in the air, and dissolves readily in half its weight of water; it is also easily soluble in alcohol; its taste and reaction are strongly acid. When heated, it abandons water, and forms two acids which will be again noticed. When a solution of it is long exposed to the air, it absorbs oxygen, and forms carbonic and acetic acids. This effect may be instantly produced by boiling it with an excess of oxide of silver, metallic silver being set free.

Tartaric acid is known by its not being volatile, and by leaving a copious coaly residue when heated. If it be fused with potash, it is decomposed, acetic and oxalic acids being produced (p. 475); with other oxidizing agents, as black oxide of manganese and sulphuric acid, it gives carbonic and formic acids. A solution of tartaric acid precipitates lime-water, but the precipitate is redissolved by an excess of acid or by solution of sal ammoniac. The soluble neutral tartrates give white precipitates, which are not crystalline, with the neutral salts of lead, lime, and silver, which all redissolve in an excess of acid.

The tartaric acid is bibasic, its formula being $C_8H_4O_{10}+2$ Aq.; several of its salts are of considerable importance.

Bitartrate of Potash. Cream of Tartar.—$C_8H_{10}O_4+$K.O.Aq.

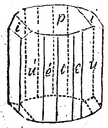
This salt, just now noticed as being deposited from grape-juice, according as alcohol is formed, is sent into commerce under the name of *Argol*, which is *red* or *white*, according to the kind of wine it was deposited from. This is dissolved in boiling water, and mixed with some pipe-clay, which, combining with the colouring matter of the grape, renders it insoluble; the clear liquor is then allowed to cool slowly, and the cream of tartar is deposited in irregular crystals on the sides of the vessel, still containing a small quantity of tartrate of lime. It crystallizes in right rhombic prisms, as in the figure, *p*, *u'*, *u* being primary, and *a*, *a'*, *i*, *m* secondary planes. It is but very sparingly soluble in cold water, requiring 80 parts at 60°, and 7 parts at 212°; hence an excess of tartaric acid produces a crystalline precipitate in solutions of potash which are not very dilute. By calcining cream of tartar either alone or with nitre, the *black* or *white fluxes* employed in metallurgy are formed (p. 334). Its

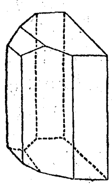


calcination furnishes also the purest source of carbonate of potash, which hence derives its name of *Salt of Tartar* (p. 487).

Neutral Tartrate of Potash. Soluble Tartar.—$C_8H_4O_{10}+K.O. . K.O.$ This salt is formed by adding cream of tartar to a hot solution of carbonate of potash, until this be completely neutralized. It crystallizes with difficulty in right rhombic prisms, which, when pure, are not deliquescent. 100 parts of water dissolve 130 parts of it at 60°, and 268 parts at 212°. Any acid added to its solution takes half the potash, and precipitates cream of tartar.

The *Tartrates of Ammonia* resemble closely those of potash. The neutral *Tartrate of Soda* crystallizes in large rhombic prisms like nitre; it is very soluble in water; its formula is $C_8H_4O_{10}+Na.O. . Na.O.+4\ Aq.$





Tartrate of Potash and Soda. Rochelle Salt, $C_8H_4O_{10}+K.O. . Na.O.+10\ Aq.$, is prepared by neutralizing a hot solution of carbonate of soda with cream of tartar: by evaporation and cooling it forms large prismatic crystals, with many sides, of the right rhombic system, *p, u, u* being primary, and *i, i, t, e, e* being secondary faces. These crystals are remarkable for being often but half formed, so as to present the aspect represented in the lower figure. Its taste is mildly saline, and not very disagreeable, whence its popularity as a medicine. It is permanent in the air except it be very dry, when it effloresces slightly at the surface; it dissolves in two parts of cold water.

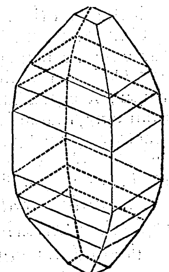
The *Tartrate of Lime* is very sparingly soluble in water, and is precipitated as a white powder, when solutions of a neutral tartrate and of a salt of lime are mixed. It dissolves in an excess of acid; and if this solution be neutralized, it is deposited in small octohedral crystals, which have the formula $C_8H_4O_{10}+Ca.O. . Ca.O.+8\ Aq.$ Nölner has asserted that, when tartrate of lime is mixed with yeast, a fermentation sets in, by which a new acid, *Pseudo-acetic Acid*, is produced; this requires, however, confirmation.

Prototartrate of Iron, $C_8H_4O_{10}+2Fe.O.$, is a white powder, very sparingly soluble in water; it is formed in minute crystals when hot solutions of protosulphate of iron and of cream of tartar are mixed together. The *Prototartrate of Iron and Potash*, $C_8H_4O_{10}+Fe.O. . K.O.$, is formed by digesting cream of tartar and water with metallic iron. Hydrogen gas is evolved, and a white, sparingly soluble salt is obtained, which, when exposed to the air, rapidly absorbs oxygen, and becomes greenish brown or black. In this state it contains magnetic oxide of iron, and is much more soluble. *Pertartrate of Iron*, formed by dissolving the freshly precipitated red oxide of iron in a solution of tartaric acid, gives by evaporation a brown jelly If the red oxide of iron be boiled with a solution of cream of tartar, it dissolves abundantly, giving a fine brown-red liquor, from which, by cautious evaporation, small ruby-red crystals may be obtained; but it is generally dried down completely, when it forms a translucent brown mass, deliquescent in damp air. An excess of tartaric acid should be avoided, as it acts on the peroxide of iron during the evaporation, reducing it to the state of protoxide, and carbonic acid being given off. Hence the pharmacopœias direct perfect neutrality of the liquor to be secured by the addition of a small quantity of ammonia. The formula of this salt is $C_8H_4O_{10}+K.O. . Fe_2O_3.$ It is very soluble in water, and its solution is not precipitated by an excess of potash.

Tartrate of Antimony.—$3(C_3H_4O_{10})+Sb.O_3.$ This salt is obtained by the solution of the sesquioxide of antimony in tartaric acid; it is colourless, and crystallizes in short deliquescent prisms.

Tartrate of Potash and Antimony. Tartar-Emetic.—$C_8H_4C_{10}+K.O. . Sb.O_3+2\ Aq.$ This salt, a most important compound of antimony, is prepared by boiling together in water equal weights of sesquioxide of antimony and cream of tartar. In the Dublin and Edinburgh pharma-

copœias, the *Powder of Algarotti* (p. 453) is employed as the source of oxide of antimony, but by the London college an impure oxide is prepared, by gently deflagrating together sulphuret of antimony and nitre with a little muriatic acid, and washing out the soluble products. In either case the oxide of antimony replaces the second atom of base (water) in the cream of tartar, and by evaporation and cooling it may be obtained in crystals, which are right rhombic octohedrons, with many secondary planes, as in the figure. This salt dissolves in fourteen parts of cold and in two of boiling water. In dry air it effloresces, losing the 2 Aq. Its solution is not affected by alkalies; but the oxide of antimony is precipitated by sulphuric or muriatic acids, and by ammonia. In the preparation of tartar-emetic, the whole product, from the materials used, can never be obtained crystallized; the mother liquor contains a substance which dries down to a transparent mass, like gum Arabic. By alcohol it is decomposed into tartar-emetic and free tartaric acid. According to Knapp's analysis, this salt is the neutral tartrate of potash and antimony, having the formula $C_4H_2O_5 . K.O.+(3C_4H_2O_5+Sb.O_3)+2$ Aq. It may be formed by dissolving tartar-emetic in a strong solution of tartaric acid, and then crystallizes in minute oblique rhombic prisms. In order to form this salt, however, from cream of tartar and oxide of antimony, a quantity of potash must enter into some form of combination, which has not been explained.



Owing to the occasional presence of arsenic in the ores of antimony, the tartar-emetic of commerce is not unfrequently contaminated by its presence, and should, in such case, be absolutely rejected from medicinal use.

If tartar-emetic be exposed to a temperature of 480°, it abandons, besides its crystal-water, two equivalents of water, the elements of which are abstracted from the constitution of the tartaric acid as generally assumed. In this dried tartar-emetic, therefore, the organic element is not $C_8H_4O_{10}$, but $C_8H_2O_8$. When redissolved in water, it resumes the two atoms of water, forming ordinary tartar emetic again. Of the other salts of tartaric acid, but one possesses this property, the borotartrate of potash being also reduced by loss of water at 480° to the formula $C_8H_2O_8+K.O. . B.O_3$. Chemists are not unanimous in explaining this peculiarity. The simplest idea is, that these two atoms of water exist ready formed in these salts, and that tartaric acid is really quadribasic; being, in its crystallized form, $C_8H_2O_8+4H.O.$; the cream of tartar being $C_8H_2O_8+K.O. . 3H.O.$; Rochelle salt, $C_8H_2O_8+K.O. . Na.O. . 2 H.O.$; and for tartar-emetic, the oxide of antimony replacing three atoms of a protoxide, the formula is $C_8H_2O_8+K.O. . Sb.O_3+2$ Aq.+2 Aq., and the two portions of water being retained by very unequal forces, are given off at very different temperatures. Berzelius considers that in this change the nature of the acid is totally altered; and as opinion is so much divided on the subject, I shall not enter farther into its discussion.

Action of Heat on Tartaric Acid.—When tartaric acid is cautiously heated, it fuses into a mass like gum, and gives off water. In this state it combines with bases, forming salts quite different from the tartrates; it retains its bibasic character, but its atomic weight is increased to one and a half times that of tartaric acid, its formula being $C_{12}H_6O_{15}+2$ Aq. It thus constitutes *Tartralic Acid;* it does not crys-

tallize, and in solution gradually passes back into tartaric acid. If the tartralic acid be kept long melted at 360°, it abandons still more water, and forms *Tartrelic Acid*, in which the bibasic character remains, its formula being $C_{16}H_8O_{20}+2$ Aq. This acid is characterized by forming insoluble salts with lime and barytes, thereby differing from the tartralic acid. If the heat be still longer kept up, a porous white mass is formed, which is insoluble in water and in alcohol. It is *Anhydrous Tartaric Acid;* its formula is $C_8H_4O_{10}$. If left long in contact with water, it changes successively into the tartrelic, tartralic, and common tartaric acid. This change is produced more rapidly by boiling with a solution of potash: this substance appears to hold the same relation to tartaric acid that the white sublimate does to the proper lactic acid (p. 536).

If tartaric acid be distilled at a still higher temperature, it abandons water and carbonic acid, and forms *Pyrotartaric Acid*, $C_5H_4O_{10}$ giving off $3CO_2$ and H.O., and $C_5H_3O_3$ remaining. The process succeeds best at about 400°. This acid is white; it crystallizes from the distilled liquors in prisms, which are to be purified from empyreumatic oil by recrystallization and digestion with animal charcoal; it reacts very acid; it melts at 210°, and sublimes at 360°; is very soluble in water and alcohol. It is a monobasic acid, forming salts which, with few exceptions, are soluble and crystallizable.

Racemic Acid.—$C_8H_4O_{10}+2$ Aq. This acid is found in grape-juice, replacing tartaric acid to a greater or less extent; its formation appears to depend on very peculiar circumstances, as it has never been found except in the district about the Vosges Mountains, and only in some seasons. It is combined with potash, forming a kind of cream of tartar, which is biracemate of potash, and from which it is prepared by the same methods as have been described for tartaric acid.

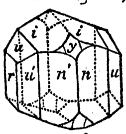
It crystallizes in colourless oblique rhombic prisms, which contain water, of which one half is lost by efflorescence in warm dry air; the remaining hydrate is identical in composition with crystallized tartaric acid; it tastes and reacts as strongly acid. In its relation to salts, it follows exactly the same rules as the tartaric acid, but their crystalline form is completely different; it is a bibasic acid, and its formula, when crystallized, is $C_8H_4O_{10}+2H.O.+2$ Aq. The characters by which it is distinguished from tartaric acid are, first, racemic acid requires ten times as much water for solution, and they are hence easily separated by crystallization. Second, that the corresponding salts are not of the same crystalline form. Third, the racemate of potash and soda is uncrystallizable, giving merely a gummy mass, while the Rochelle salt forms very large crystals. Fourth, the racemate of lime is insoluble in a solution of sal ammoniac. The two acids, however, form a most perfect example of isomerism, as not merely their composition, but their atomic weight is absolutely the same.

When heated, racemic acid passes through precisely the same changes as have been described for tartaric acid, abandoning water, and forming bibasic acids, whose formulæ are respectively $C_{12}H_6O_{15}+2H.O.$ and $C_{16}H_8O_{20}+2H.O.$ They are distinguished by their salts, which differ in characters from each other, and from those of the bodies formed by tartaric acid.

By the destructive distillation of racemic acid is generated the *Pyroracemic Acid*, in which the isomerism with the tartaric acid series is broken through; its formula being $C_6H_3O_5$. It differs totally in properties from the pyrotartaric acid; it does not crystallize; it tastes acid; its salts are all soluble and crystallizable, but pass also into a gummy condition. If a little crystal of copperas be laid in a solution of one of these salts, it becomes coloured bright red.

Citric Acid.—$C_{12}H_5O_{11}+3H.O.+2$ Aq.

This acid exists in the juices of fruits, especially the lemon, orange, currant, and quince. It is usually prepared from lemon-juice, which is clarified by rest, then saturated with chalk, and the neutral solution is boiled until the citrate of lime is completely deposited; this is then washed and decomposed by a quantity of oil of vitriol, equal in weight to the chalk employed, and diluted with six volumes of water. After the sulphate of lime has been removed by straining, the liquor is evaporated, and allowed to crystallize by very slow cooling; its form is generally that of a right rhombic prism, very much modified, as in the figure, where *i*, *u'*, *u* are primary, and *n'*, *y*, *r* are secondary planes. In this case its formula is that given above; but if its solution be evaporated at 212° to a pellicle, it crystallizes while hot in a totally different form, and its formula is then $C_{12}H_5O_{11}+3H.O.$ By exposing the hydrated crystals in vacuo to sulphuric acid or to a gentle heat, the 2 Aq. may also be removed.



The citric acid possesses an agreeably sour taste; it dissolves in less than its own weight of cold, and in half its weight of boiling water; it is sparingly soluble in alcohol; when heated, it fuses, becomes yellow, and ultimately gives the usual pyrogenic products of organic acids. It is a tribasic acid, and gives rise to three classes of salts; and, as these contain different quantities of combined water, their history was very confused until Liebig explained their true constitution. Very few of these salts are, however, of practical or medicinal interest.

Citrate of Soda crystallizes in efflorescent prisms, having the formula $C_{12}H_5O_{11}+3Na.O.+4$ Aq.$+7$ Aq. By exposure to a heat of 212° the 7 Aq. are removed, and at 400° the remaining 4 Aq. are driven off: Berzelius is of opinion that in this action the real constitution of the citric acid is changed, and that it is partly converted into aconitic acid; but the point is not yet experimentally decided, and Liebig's views explain the phenomena with such beautiful simplicity, that I have no hesitation in adopting them, at least provisionally.

The *Citrate of Lime* is obtained by mixing solutions of a soluble citrate and of a salt of lime; it forms a white powder, sparingly soluble in pure water, but much more so if the liquor be acid. Its constitution is $C_{12}H_5O_{11}+3Ca.O.+4$ Aq. When boiled with an excess of lime-water, citric acid forms a *basic Citrate of Lime*, which is less soluble than the neutral salt.

The *Citrates of Lead and of Barytes* are white powders, insoluble in water, formed by double decomposition, and resembling in constitution the citrate of lime; there are also basic salts, the formation of which, as in that of lime, appears to result from the crystal-water (2 Aq.) of the acid being more or less replaced by metallic oxide, in addition to that which fulfils the proper basic function.

The citric acid is easily recognised by forming no precipitate with lime-water unless the liquor be heated. Its potash salt is also very soluble, even with an excess of acid; it is thus distinguished from the racemic and tartaric acids.

When citric acid is heated, it fuses, gives off water, and is converted into an acid, which, from being found in the aconitum napellus, is called *Aconitic Acid*, but it exists also abundantly in various species of equisetum, and is hence often called *Equisetic Acid*. To complete the change of the citric acid, it must be distilled until the gases which come over cease to be inflammable, and oily drops appear in the receiver; the process is to be then interrupted, the mass remaining in the retort to be dissolved in water, the solution filtered and evaporated to a pellicle. On cooling, it forms a crystalline mass, from which ether dissolves out the aconitic acid, and leaves unaltered citric acid behind; the former may then be obtained crystallized by evaporation.

Aconitic acid is soluble in water, alcohol, and ether; its formula is $C_{12}H_3O_9+3$ Aq.; like citric acid, it is tribasic; it forms well-characterized salts: the aconitate of ether had been mistaken for citric ether; for, when citric acid is put in contact with alcohol and oil of vitriol, it changes into aconitic acid.

If aconitic acid be heated until it boils, it gives off carbonic acid, and forms *Itakonic Acid*, which distils as an oily liquid, and forms a crystalline mass as it cools; by solution in alcohol and slow evaporation, it may be obtained in long prismatic needles; its salts, of which there are two classes (it being bibasic), generally crystallize very well; its formula is $C_{10}H_4O_6+2$ Aq.; formed by the aconitic acid losing C_2O_4, but an atom of water, previously basic, entering into the organic element. When the *Itakonic Acid* is redistilled, it is converted into water and a heavy oily liquid, *Citrakonic Acid*, the formula of which is $C_{10}H_3O_5+$Aq. In contact with water, it forms a crystalline mass containing 2 Aq.

All these products are simultaneously and successively formed in the distillation of common citric acid. Acetone is also generated, $C_{12}H_{12}O_{12}$ giving $3(C_3H_3O.)$, with $3H.O.$ and $3(C.O_2)$.

Malic Acid.—$C_8H_4O_8+2H.O.$

This acid exists in most fruits, associated with citric and tartaric acids, but is found purest and most abundant in the berries of the mountain ash and in the houseleek. The best mode of extraction is the following, devised by Liebig. The juice of the berries of the mountain ash (sorbus aucuparia) is to be nearly, but not completely, neutralized by lime, and the liquor then boiled for some hours, during which the malate of lime precipitates as a sandy white powder; when no more falls down, the neutralization is completed by adding a little more lime, and on cooling, the remainder of the salt is obtained. This malate of lime is to be dissolved by boiling in the smallest possible quantity of very dilute nitric acid. On cooling, the acid malate of lime crystallizes, and is to be purified by recrystallization. This salt being then decomposed by acetate of lead, malate of lead is formed, which, being acted on by sulphuretted hydrogen, gives sulphuret of lead and free malic acid; by evaporation of the liquor and cooling, a sirup-thick liquid is obtained, which, after long repose, forms a white crystalline mass.

Malic acid is deliquescent, and very soluble in water. It tastes and reacts strongly acid; its relations to bases are very curious; thus magnesia is the only earth by whose carbonate it can be completely neutralized. This arises from its tendency to form salts, in which one atom of basic water is preserved, it being a bibasic acid. Another peculiarity pointed out by Hagen is, that it forms with many bases two neutral salts, of which one retains water with obstinacy at 212°, at which temperature the other at once abandons it. When crystallized it appears to contain only basic water; its formula is hence $C_8H_4O_8+2$ Aq. None of its salts are of technical or medicinal interest, and hence require but brief notice.

The alkaline malates are very soluble in water, scarcely crystallizable, sparingly soluble in alcohol.

The *Malate of Lime* forms as a granular white precipitate when malic acid is neutralized by lime. Its formula is $C_8H_4O_8+2Ca.O.$; it separates in hard, brilliant crystals, which contain 5 Aq., when the following salt is neutralized by an alkaline carbonate. *Bimalate of Lime*, $C_8H_4O_8+Ca.O.\ .\ H.O.+6$ Aq., crystallizes in large right rhombic octohedrons. Water dissolves it abundantly when boiling, but very sparingly when cold.

The *Malate of Lead*, $C_8H_4O_8+2Pb.O.$, precipitates, on mixing solutions of a soluble malate with acetate of lead, as a white curdy mass, which, after some time, changes into minute but brilliant crystalline scales. By boiling in water, a small quantity of it is dissolved, which separates in brilliant plates on cooling. It fuses below 212°, and is then nearly insoluble in water.

Malic acid is distinguished both from tartaric and citric acids by not giving any precipitate with lime-water either by heat or when cold.

When malic acid is heated to a temperature of about 400°, it abandons water and

gives origin to two acids, of which one is remarkable as being found naturally existing in several plants. They are the *Maleic Acid* and the *Fumaric Acid*, the latter so called from having been first discovered in the fumaria officinalis. These acids are isomeric, the reaction being in both cases that $C_8H_4O_8$ produces 2H.O. and $C_8H_2O_6$. Both acids may be formed in the same process; the maleic acid passes over with the water, and crystallizes from the condensed liquor; the less volatile fumaric acid constitutes the residue in the retort, which solidifies into a crystalline mass as it cools. From the plants which contain this acid, it may be obtained by precipitating the clarified juices by acetate of lead, and decomposing the salt of lead by sulphuretted hydrogen. The liquors yield the acid by crystallization when concentrated to the necessary degree.

The *Maleic Acid*, which had been thought identical with the *Aconitic Acid*, already noticed, forms crystals of a sour, bitter taste, soluble in water, alcohol, and ether. When heated, it abandons water, and the anhydrous acid remains, which, if the water be allowed to flow back, gradually changes into fumaric acid. This anhydrous acid melts at 167°, and sublimes at 350°. Of its salts, that of barytes alone is remarkable; it is a white precipitate, which changes soon into a mass of brilliant plates.

The *Fumaric Acid*, which exists also in Iceland moss, crystallizes in fine long prisms, which fuse with difficulty, and volatilize first at 400°. It requires 200 parts of water for its solution. When heated, it is decomposed into water and anhydrous maleic acid. The fumarate of silver is so insoluble, that one part of the acid, dissolved in 200,000 parts of water, is precipitated by nitrate of silver, but the precipitate dissolves in nitric acid. The salts, with copper, iron, and lead, are also very sparingly soluble.

When muriatic acid gas is passed into a solution of malic acid in absolute alcohol, Hagen found that the ether formed contains fumaric, and not malic acid. It is a liquid, heavier than water, of an agreeable smell. With potash it gives alcohol and fumarate of potash. Its formula is $C_4H.O_3+Ae.O.$ On adding water of ammonia to this ether, a substance is deposited in brilliant white scales, insoluble in cold water and in alcohol, but dissolved by boiling water. It is *Fumaramid*, its formula being $C_4H..O_2Ad$. By potash, ammonia is set free, and fumarate of potash formed.

Meconic Acid.—$C_{14}H.O_{11}+3H.O.+2$ Aq.

This acid is found only in opium; it is best extracted by adding chloride of calcium to an infusion of opium in cold water. A white precipitate of mixed meconate and sulphate of lime occurs. This, being washed with hot water and with alcohol, is to be treated with dilute muriatic acid, heated to about 180°. The meconate of lime dissolves, and, from the liquor on cooling, bimeconate of lime separates in brilliant crystalline plates. On dissolving these in warm, strong muriatic acid, and cooling the solution, the pure meconic acid crystallizes. It may be freed from any adhering colouring matter by combination with potash, decomposing the crystallized meconate of potash by muriatic acid, and recrystallization.

When pure, meconic acid is in brilliant white crystalline scales, containing 2 Aq., which they give off at 212°; it is soluble in four parts of boiling water; it is a tribasic acid, forming salts, of which those with the earths and heavy metallic oxides are generally insoluble in water. There are three classes of *Meconates*, according as the quantity of fixed base is one, two, or three atoms. Few of them are specifically of importance. The most characteristic properties of this acid are, 1st, that it produces with solutions of the peroxide of iron a blood-red colour, analogous to that of the sulphocyanide of iron, from which it is distinguished by the fact that, on the addition of the acetate of lead, a white precipitate is formed, which, when heated to full redness with a little sulphur and potassium, and treated with water, gives no red colour with the salts of iron (see page 525); 2d, that with nitrate of silver it gives a white precipitate, which is dissolved by dilute nitric acid; the liquor, however, when boiled, becomes milky, and deposites cyanide of silver.

If a strong solution of meconic acid be boiled for a long time, or if the crystallized acid be dissolved in strong, boiling muriatic acid, it is converted into *Komenic Acid*, carbonic acid being given off. The crystallized meconic acid undergoes the same change when heated to 400°. This acid forms granular crystals, which are soluble only in sixteen parts of boiling water, and have the formula $C_{12}H_2O_8+2H.O.$, as the $C_{14}H.O_{11}$ loses C_2O_4 and gains H.O. This acid is bibasic; the third atom of water, which was basic in the meconic acid, entering into the radical here. It also red-

dens the per-salts of iron. It forms two series of salts, which in properties resemble closely the corresponding meconates. When it is heated to 500°, it gives off water and carbonic acid, and forms *Pyromekonic Acid*, of which the formula is $C_{10}H_3O_5+H.O.$ This acid forms crystalline plates, which fuse at 240°, and are volatilized by a heat little higher. It is very soluble in water, alcohol, and ether; it is a monobasic acid, forming salts, which, with the exception of that of lead, are all soluble in water. Like the acids from which it is derived, it strikes a blood-red colour with solutions containing peroxide of iron.

Tannic Acid, or *Tannin*.—$C_{18}H_5O_9+3H.O.$

This important substance exists in the bark of most exogenous trees, particularly the oak and horse-chestnut, accumulated principally in the inner layers of bark. It is found also in the roots of the tormentilla and bistort, in the leaves of roses and pomegranates; but its most abundant source is the gall-nut of the oak (quercus infectoria).

To distinguish this from the other kinds of tannin, of which there is a great number, it may be suitably termed *Gallo-tannic Acid*, and I shall generally, though, perhaps, not uniformly, employ that name.

The method given by Pelouze for its extraction, and which serves for the preparation of a variety of other vegetable principles, is as follows:

Into a globular funnel, *b*, which can be closed at the top by a stopper, and rests in a bottle, *a*, as in the figure, is to be introduced a quantity of nut-galls in powder, moderately compressed, after the tube of the funnel has been stopped with a little cotton. The upper empty part of the funnel is to be then filled with ether, as it is usually in the shops, containing about one tenth of water dissolved in it, and the apparatus allowed to stand for some days. The bottle is then found to contain two layers of liquid. The inferior, sirup-thick, is a concentrated solution of tannic acid in water, with very little ether. The upper is ether, containing but a trace of tannic and gallic acids. Being separated, the lower layer is to be washed once or twice with a little ether, and then evaporated in vacuo with a capsule of sulphuric acid. A faintly-yellowish white mass remains, of a distinctly crystalline structure, which is pure gallo-tannic acid. The theory of this process is, that the tannic acid is so greedy of water as to withdraw it from the ether, and to dissolve it to the exclusion of every other constituent of the gall-nut.

The watery solution of gallo-tannic acid reddens litmus; it is probably insoluble in absolutely anhydrous alcohol and ether; its taste is intensely astringent, but not bitter. The most characteristic property of tannic acid is, that it combines with the animal substance *Gelatine*, and forms a compound insoluble in water, which is the basis of most kinds of leather; hence any tissue, as skin, which contains gelatine, removes gallo-tannic acid from its watery solution, on which is founded the art of *Tanning*. It is a tribasic acid, and forms three classes of salts, which are of interest from the colours of precipitates it gives with metallic solutions, being often useful as a test for the presence of certain metals. Hence an *infusion*, or *tincture of Galls*, is always found in the laboratory as a reagent; it does not affect the solutions of *Zinc* or *Cadmium*, or the *protoxides of Iron* and *Manganese*, nor any of the alkaline or earthy salts. With the other metals it gives precipitates which, with *Lead* and *Antimony*, are white; with *Copper*, gray; with *Tin*, *Nickel*, *Cobalt*, *Cerium*, *Tellurium*, and *Silver*, are various shades of yellow; with *Tantalum* and

Bismuth, are orange; with *Titanium*, blood-red; with *Platinum*, green, with *Chrome*, *Molybdenum*, *Uranium*, and *Gold*, are brown; and with *Osmium* and *peroxide of Iron*, are rich bluish purple. This last is the most important of all, from its great delicacy and distinctness. If the solutions be very strong, the liquor appears absolutely black, and constitutes the material of ordinary writing ink.

The insolubility, and consequent inactivity of tartrate of antimony, is taken advantage of in medicine, infusion of oak-bark or galls being employed as an antidote in poisoning by tartar-emetic. I shall have occasion hereafter to notice its use in the detection and neutralization of the vegetable alkaloids.

The gallo-tannic acid is not the only kind of tanning material employed in the manufacture of leather; yet, as the others will hereafter come under notice, I shall give Humphrey Davy's estimate of the comparative power of such substances as contain true tannic acid. He found the quantity of active material in 100 parts of the following bodies to be,

Gall-nuts	27·4	White inner oak bark	16·0
Oak bark entire	6·3	White inner horse-chestnut	15·2
Horse-chestnut bark entire	4·3	Sicilian sumach	16·2
Elm bark entire	2·7	Malaga sumach	10·4

These numbers are but approximative, and such as are given by very rough processes, the true quantity of tannic acid present being much larger; thus the gall-nuts easily yield, by Pelouze's method, forty per cent of pure product.

When a solution of tannic acid is exposed to the air, it is decomposed, absorbing oxygen and evolving carbonic acid, the liquor becomes coloured, and a large quantity of gallic acid is found to be produced.

Gallic Acid.—$C_7H.O_3+2H.O.+Aq.$

This remarkable substance does not appear to exist naturally formed in plants, but is generated by the decomposition of gallo-tannic acid. Powdered galls are to be made into a thin paste with water, and exposed to the air for some weeks, at a temperature of about 80°, water being supplied according as it evaporates away; the resulting mass is to be boiled with water, and the gallic acid crystallizes out of the liquor as it cools. By digestion with ivory black and recrystallization, it is obtained completely pure.

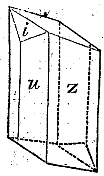
In this process the reaction is very simple, as an atom of tannic acid, $C_{18}H_8O_{12}$, absorbing from the air eight atoms of oxygen, produces $4C.O_2$ and $2(C_7H.O_3+3\ Aq.)$.

The conversion of gallo-tannic acid into gallic acid may occur, however, without the access of air, and, indeed, be effected almost instantaneously; thus, if tannic acid be boiled in a strong solution of potash for a few minutes, and an excess of sulphuric acid be then added, a copious product of gallic acid is obtained crystallized on cooling; or, if sulphuric acid be added to a strong solution of gallo-tannic acid, and the precipitate thus formed be washed with a small quantity of water, and then added gradually to boiling dilute sulphuric acid, it dissolves, and on cooling the gallic acid crystallizes. In these reactions, which succeed also perfectly with infusion of galls, some other substances must be simultaneously formed, which are as yet not known. Gallo-tannic acid contains exactly the constituents of gallic acid and acetic acid, as $C_{18}H_5O_9=2(C_7$

$H.O_3)+C_4H_3O_3$; but Liebig has determined that acetic acid is not produced.

This change may occur in the nut-gall itself, which it is very probable contains a principle analogous to yeast, which, under favourable circumstances, induces this kind of decomposition in the gallo-tannic acid. This idea, first suggested by Robiquet, has derived much support from the experiments of Larocque, who found that the matter of the nut-gall which remains after the extraction of the tannin has the power of exciting the alcoholic fermentation in solutions of sugar. As yet, however, we possess no accurate knowledge of the theory of this interesting transmutation.

Pure gallic acid crystallizes in colourless oblique rhombic prisms, as ***u, z*** in the figure, where *i* is a secondary plane; it tastes bitter and slightly acid, and requires 100 parts of cold, but much less of boiling water for its solution; it is less soluble in alcohol; its crystals contain three atoms of water, of which one is expelled at a temperature of 230°, but the remaining two are only removed when replaced by bases. It is a bibasic acid, forming two classes of salts; those with the alkalies are very soluble; the earthy and metallic salts are insoluble in water. With a per-salt of iron, gallic acid gives a blackish-blue precipitate, which differs from the tannate of iron in becoming gradually colourless, the acid being decomposed, and the iron reduced to the state of protoxide; this is effected instantly by boiling, carbonic acid gas being evolved. The gallic acid is farther distinguished from the tannic by not precipitating gelatine nor any of the vegetable alkalies.



Products of the Decomposition of Gallic Acid.

Pyrogallic Acid.—When gallic acid is carefully heated to about 400°, it is totally decomposed into carbonic acid and pyrogallic acid ($C_7H_3O_5=C_6H_6O_3+C.O_2$), which sublimes in brilliant white plates; it is easily soluble in ether, alcohol, and water; it reacts feebly acid; it fuses at 240°, and sublimes at 400°. If a solution containing peroxide of iron be added to a solution of pyrogallic acid, a black colour is struck, but the iron is rapidly reduced to the state of protoxide, and the liquor assumes a rich red tint. If, however, a salt of pyrogallic acid be used, the solution remains permanently blue.

Melangallic Acid.—If, in the distillation of pyrogallic acid, the temperature be allowed to rise beyond 450°, it is decomposed, water is given off, and a shining, jet-black mass, like coal, remains in the retort, which is this body; its formula is $C_{12}H_3O_3$, being formed from $2(C_6H_3O_3)$ by loss of 3H.O.; it is insoluble in water, alcohol, and ether; at a temperature of 500° it is totally decomposed into the ordinary pyrogenic products; it dissolves in alkaline solutions, forming salts of a black colour, which do not crystallize; these salts give black precipitates with solutions of the earthy and metallic salts.

If gallo-tannic acid be heated to about 400°, it is resolved totally into pyrogallic, melangallic, and carbonic acids and water.

Ellagic Acid.—In the formation of gallic acid by the slow fermentation of tannic acid, a certain quantity of ellagic acid generally, though not constantly, appears. Being insoluble in water, it remains when the gallic acid has been dissolved out; and, by digesting the residue with a weak solution of potash, it is taken up, and may then be precipitated by muriatic acid.

It forms minute crystals, whose formula is $C_7H.O_3+H.O.+Aq.$ The Aq. is driven off by a heat of 212°, and the dry acid is then isomeric with the gallic acid, but it is monobasic; it is very feebly acid, not expelling carbonic acid from its salts; the earthy and metallic *Ellagates* are all insoluble, and all white or yellow.

If gallic acid be heated to 280° with oil of vitriol, it dissolves, and on cooling, brilliant crystals of a dark scarlet colour are deposited, which constitute *Parellagic Acid.* This body is isomeric with ellagic acid; it forms with bases salts which are

generally red. It is worthy of notice, that ellagic acid acted on by oil of vitriol gives no parellagic acid.

It is here probably best to notice the formation of what has been termed *Artificial Tannin;* it is produced by mixing one part of almost any kind of vegetable substance with five parts of oil of vitriol, letting the mixture stand for some days, and then heating it as long as any sulphurous acid gas is evolved. A black mass remains, from which the remaining acid is to be washed with water, and then the tannin dissolved out by alcohol; the solution is dark brown, and when evaporated gives a black extractive matter, which tastes astringent, smells of burned sugar, and dissolves in water; it precipitates gelatine, but does not affect the salts of iron like true tannin.

Another and a very singular manner of producing artificial tannin consists in boiling pure charcoal in nitric acid as long as any reaction occurs; the liquor is then brown; being evaporated to the consistence of a sirup and mixed with water, a brownish-yellow substance falls, and the filtered solution gives, by evaporation, a hard black mass, which reddens litmus, tastes astringent, is soluble in water and alcohol, and copiously precipitates gelatine; when heated, it smells like horn, and contains nitrogen; it precipitates most metallic salts brown. The true nature of these bodies is not well known, as they have not been much studied since the methods of organic chemistry acquired their present exactness; they are probably mixtures of many bodies, as ulmine in its various forms with crenic and aprocrenic acids.

Catechuic Acid and Catechutannic Acid.

The *Catechu*, or *Terra Japonica*, a brown extract prepared from the wood of the mimosa catechu, appears to contain at least four acids, the precise composition and connexion of which have not yet been definitely established. The rough catechu, as imported, is of extensive use in medicine, and in the arts for tanning and for giving a rich permanent brown dye. Davy estimated that 100 parts of Bengal catechu contain forty-eight, and of Bombay catechu about fifty-four per cent. of useful tanning material.

If catechu be treated with ether, by the method of displacement as described for tannic acid, the liquor does not separate into two layers, but a strong solution of *Catechutannic Acid* in ether is obtained, which, by evaporation, yields it as a pale yellow, scarcely crystalline mass, in taste and appearance similar to tannic acid; its solution in water precipitates gelatine, but not tartar-emetic; with the salts of peroxide of iron it strikes an intensely olive-green colour, which is best marked with the perchloride, being somewhat purple with the persulphate; exposed to the air, its solution rapidly absorbs oxygen, becomes red, and finally brown, depositing a brown insoluble matter. This change is instantly effected by any oxidizing agent.

The catechutannic acid has been analyzed by Pelouze, who ascribes to it the formula $C_{18}H_8O_8+Aq.$; it would thus appear to be formed by the abstraction of four atoms of oxygen from tannic acid.

When catechu has been deprived of the catechutannic acid by ether or continued washings with cold water, the residual mass is to be boiled in alcohol, and the filtered liquor evaporated to one third of its volume; on cooling, *Catechuic Acid* crystallizes. If coloured, it is to be dissolved in boiling water, precipitated by acetate of lead, the catechuate of lead diffused through boiling water, and decomposed by sulphuretted hydrogen; the liquor being filtered, gives, on cooling, a perfectly white and pure catechuic acid; it forms satiny flakes, indistinctly crystallized; it is very little soluble in cold water, but abundantly in boiling water and in alcohol; it is insoluble in ether; its solution is not acid; it appears to exist in very different states of hydration, or, possibly, different kinds of catechu contain substances which are totally distinct, for the formulæ assigned to it are quite discordant, and chemists are not agreed quite as to its properties. Svanberg, who examined the catechu from the mimosa catechu, gives as its formula $C_{15}H_5O_5+Aq.$ Zwenger, who states the substance he worked with to be the produce of the nauclea gambir, gives

$C_{20}H_9O_8+Aq.$; and Hagen, who used Bengal catechu, found the catechuic acid to be $C_{14}H_6O_6+3$ Aq., and its lead salt $C_{14}H_6O_6+2Pb.O$. Additional researches are required to clear up this confusion.

When catechuic acid is heated, it fuses, gives off water, and, finally, a white crystalline sublimate, *Pyrocatechin*, which has the formula $C_6H_2O.+Aq.$, its characteristic property is that of forming a bright green solution with alcohol.

If a solution of either of the acids now described be exposed to the air, oxygen is absorbed, and much more rapidly in presence of an alkali. The substance formed is termed *Japonic Acid;* it makes up the mass of the coloured portion of catechu; it is almost insoluble in water; soluble in caustic, but not in carbonated alkalies. Svanberg gives for it the formula $C_{12}H_2O_4+Aq.$ If catechuic acid be boiled with a solution of carbonate of potash, *Rubinic Acid* is formed, whose formula is said to be $C_{18}H_6O_9$. By farther absorption of oxygen it forms japonic acid. None of these results, however, can be considered as definitely established.

Cinchonatannic Acid and Cinchonic Acid.

These substances exist in the barks of various species of cinchona, combined with quinia and cinchonia. The first is extracted by digestion in dilute muriatic acid and precipitation with magnesia. The precipitate is to be dissolved in acetic acid and precipitated with acetate of lead, which leaves the alkaloids dissolved; the cinchonatannate of lead being decomposed by sulphuretted hydrogen, the filtered liquor yields, on evaporation, the *Cinchonatannic Acid* pure, and of a very pale yellow colour, not crystalline. In properties it resembles closely ordinary tannic acid; it precipitates gelatine and tartar-emetic. An infusion of cinchona is hence recommended as an antidote in cases of poisoning by tartar-emetic. It colours solutions of the per-salts of iron green. By exposure to the air, it is converted into a rust-coloured substance termed *Cinchona Red.* Nothing is known of the composition of these bodies.

The *Cinchonic Acid*, which Berzelius believes to exist in the inner bark (albumen) of fir and of most trees, is obtained by adding lime in small quantity to a cold infusion of cinchona bark. The alkaloids being thus separated, the liquor is filtered and evaporated very carefully to the consistence of a sirup. On standing for a few days, the cinchonate of lime crystallizes in needles, which are to be decomposed by an exact equivalent of sulphuric acid. The gypsum being removed by the filter, the solution is concentrated, and the cinchonic acid crystallizes. It forms small acid needles; is very soluble in water; its salts are all soluble in water; it affects neither gelatine, tartar-emetic, nor the per-salts of iron; its formula appears to be $C_{14}H_8O_8+4$ Aq. When it is heated, a substance sublimes in brilliant yellow needles, which is termed *Chinoyl*, and consists of $C_3H.O$.

Kinoic Acid, or *Coccotannic Acid.*

The substance known in pharmacy as *Gum Kino*, which is an extract of the wood of the coccoloba uvifera, is to be dissolved in cold water, the solution precipitated by sulphuric acid, the precipitate washed, dissolved in boiling water, and solution of barytes added until the sulphuric acid is all removed; the liquor is then carefully evaporated to dryness. The kinoic acid forms a crimson transparent mass, soluble in alcohol and water, but not in ether; its taste is astringent, but not bitter. The salts of this acid are not known, nor has its composition been examined. It does not precipitate solution of tartar-emetic.

Of the following acids we possess little more than a knowledge of their probable existence.

Lactucic Acid is said to exist in the lactuca virosa. The expressed juice is precipitated by acetate of lead, and the lactucate of lead decomposed by sulphuretted hydrogen. From the liquor the acid crystallizes by evaporation and cooling, like oxalic acid; it tastes acid, and gives with protosalts of iron a green, and with salts of copper a brown precipitate.

Fungic Acid exists in most mushrooms; their expressed juice is boiled, and the coagulated albumen removed by filtration; the liquor is then evaporated to a sirup, and treated with alcohol. Fungate of potash remains undissolved, from which the acid is obtained by acetate of lead and sulphuretted hydrogen. The fungic acid is colourless, sour, deliquescent, and not crystalline.

Boletic Acid is obtained from the boletus ignarius, in the same way as the last acid is from other mushrooms. It crystallizes readily, and sublimes without decomposition.

Krameric Acid exists in rhatany root (krameria triandria). The watery infusion is precipitated, first by gelatine, and then by copperas. The filtered liquor is concentrated, neutralized by lime, precipitated by acetate of lead, and the kramerate of lead decomposed by sulphuret of hydrogen; it crystallizes irregularly, and tastes strongly acid and astringent; its formula is probably $C_{10}H_8O_5$, by Liebig's analysis.

Caïncic Acid exists in the root of the chiococca racemosa. Its mode of extraction resembles that of the krameric acid; it crystallizes in needles; is but sparingly soluble in water; its solution reacts acid; it appears to have the same formula as krameric acid, and perhaps they are really identical.

Verdous and Verdic Acids exist in a variety of plants of the families dipsaceæ, compositæ, and eupatoriæ; it is best prepared from the roots of the scabiosa succisa. They are to be digested in alcohol, and the solution mixed with ether. Impure verdous acid is thrown down; it is to be dissolved in water, and the liquor precipitated by acetate of lead; the verdite of lead being collected and decomposed by H.S., gives the pure *Verdous Acid*, which remains after evaporation as a clear yellow mass, which is not altered by the air; it reddens litmus strongly. If it be neutralized by an alkali, it then absorbs oxygen rapidly, and the solution becomes deep green; from this, acids throw down a brown-red powder, which is *Verdic Acid*. Runge, who observed these facts, considers that the two acids are different oxides of the same radical, but no exact researches have been made about them.

Other acids, of which the existence has been only indicated, will be noticed in describing the more important bodies with which they are associated in the plants.

CHAPTER XXV.

OF THE NEUTRAL ORGANIC SUBSTANCES AND THE PRODUCTS OF THEIR DECOMPOSITION.

The bodies to be described in this chapter are distinguished by the absence of distinct acid or basic characters, and also that they are at least so destitute of colour as not to be included in the list of colouring matters. In other respects they possess no direct connexion with each other, and are united only for convenience of arrangement.

Pectin, or *Vegetable Jelly.*

This substance, which is to be carefully distinguished from animal jelly, or *Gelatine*, to which it by no means bears the relation that the albumen of plants does to that of animals, is very extensively diffused, being found in almost every kind of plant, and distributed through all their parts. It is very easily prepared from the expressed juice of white beet, celery, parsley, currants, cherries, or plums. It is sufficient to filter the juice and mix it with alcohol; after some hours, the pectin separates as a consistent jelly, which is to be collected on a filter, washed with alcohol, and dried by a very moderate heat. It forms a transparent mass, like isinglass, and is almost insipid. When immersed in water, it swells up; one part gives a firm jelly with 100 parts of water. When acted on by nitric acid, it produces pectic and the mucic acid. It precipitates the salts of barytes, lead, copper, and sesquioxide of iron, but does not affect solutions of silver, of protosulphate of iron, of tartar-emetic, of tannic acid, or of silicate of potash. Its formula, as from the experiments of Fremy, is $C_{24}H_{17}O_{22}$. By long boiling, or by contact with any powerful acid or base, it changes into the following substance:

Pectic Acid appears to exist naturally combined with lime in many plants, and is precipitated from their juice on the addition of muriatic acid. The precipitate is to be boiled with a little lime, and the solution again decomposed by muriatic acid. The pectic acid, which then separates pure, is to be washed with distilled water and dried. It does not crystallize, but forms white transparent scales, tastes distinctly acid, and reddens litmus. It dissolves very sparingly in cold, but more copiously in boiling water; the solution is colourless, and does not gelatinize on cooling, but is coagulated to a transparent jelly by acids, by lime-water, alcohol, and many salts. Sugar gradually converts the solution into a firm jelly, and is thus useful in the manufacture of the preserves of juicy fruits.

The pectic acid is isomeric with pectin, its formula being $C_{24}H_{17}O_{22}$. It appears to be bibasic, the pectate of lead being $C_{24}H_{17}O_{22}+2Pb.O$. Its alkaline salts are soluble in water, but the others are insoluble, and form transparent jellies while moist.

If pectin or pectic acid be boiled in a solution of potash, the alkali being in excess, until the liquor ceases to give any precipitate on the addition of muriatic acid, *Metapectic Acid* is formed. On the addition of sugar of lead, metapectate of lead is thrown down, which, being decomposed by sulphuretted hydrogen, the metapectic acid dissolves, and is obtained by cautious evaporation to dryness. Its taste and reaction are strongly acid; it deliquesces, and dissolves easily in alcohol and water; it is not volatile. When dry, it is isomeric with the preceding bodies, its formula also being $C_{24}H_{17}O_{22}$; but its salts contain five atoms of base. Those of the alkalies are soluble and uncrystallizable, but those of the earths and heavy metallic oxides are insoluble in water.

Of Salicine, and the Bodies derived from it.

This substance exists in the leaves and bark of a great variety of trees, but is particularly abundant in those species of salix which have a bitter taste. The bark is to be boiled three or four times with water, the decoction evaporated till it amounts to but three times the weight of the bark employed, then digested for twenty-four hours with oxide of lead, and the clear liquid evaporated to the consistence of a sirup. After a few days this becomes a mass of crystalline fibres, which, separated by pressure from the mother liquor, are to be purified by solution, digestion with animal charcoal, and recrystallization.

When pure, salicine is in the form of small white rectangular crystalline plates or prisms; its taste is very bitter. It dissolves in eighteen parts of cold and in one of boiling water; it is soluble in alcohol, but not in ether; at 212° it melts, and on cooling solidifies into a crystalline mass. The composition of salicine has been very accurately determined; its formula is, when crystallized, $C_{21}H_{12}O_9+2$ Aq.; it precipitates the basic acetate of lead, forming a white compound, the formula of which is $C_{21}H_{12}O_9+3Pb.O$.

The products of the decomposition of salicine are exceedingly remarkable. When it is boiled with dilute sulphuric acid, it is decomposed into grape-sugar, and a resinous substance termed *Saliretine*. Three atoms of salicine, $C_{63}H_{36}O_{27}$, giving saliretine, $C_{51}H_{24}O_{15}$, and sugar, $C_{12}H_{12}O_{12}$. When quite pure, this body is white or pale yellow. It is insoluble in water, but soluble in alcohol and ether.

With sulphuric acid and chromate of potash, salicine gives hydruret of salicyl (oil of spiræa), as described page 573. Although the evolution of formic and carbonic acids, which occur in this reaction, show that it is in reality complex, yet its result may be expressed by the simple abstraction of water from the salicine, as $2(C_{21}H_{12}O_9)-6H.O.=3(C_{14}H_6O_4)$.

When salicine is boiled with nitric acid, it is totally converted into picric acid. As this body is, however, more closely connected with indigo, it will be there fully described.

By the action of chlorine on salicine two bodies are produced, one crystalline, whose formula is $C_{21}H_{12}$ Cl_2O_9, and the other a heavy oil, consisting of $C_{21}H_8$. Cl_4O_9. They are both soluble in alcohol, but sparingly soluble in water.

If strong oil of vitriol be poured on salicine, it is decomposed into water and a

deep olive-green powder, *Olivin*, the formula of which is $C_{21}H_9O_6$. This action is accompanied by the disengagement of much heat. Olivin is crystalline, insoluble in water, alcohol, and ether. If the oil of vitriol be in great excess, it becomes red-coloured, and the salicine dissolves. The red substance thus formed is termed *Rufin*; it is obtained more simply from phloridzine. If a large quantity of salicine be acted on by sulphuric acid, it forms a tenacious mass, which, when treated with water, and the liquor neutralized by lime, gives a brown resinous body, which is termed *Rutilin*. This contains sulphuric acid, its formula being $C_{23}H_{12}O_4+S.O_3$.

Of Phloridzine and its Products.

This remarkable substance exists in the bark of the roots of the various species of apple, pear, plum, and cherry trees. It is prepared by infusing the root-bark in weak spirit for eight or ten hours at 120°. The greater part of the spirit may then be distilled off, and on cooling, the phloridzine crystallizes from the remaining liquor. It forms brilliant silky plates and needles, perfectly white when pure. It is easily soluble in alcohol, ether, and in boiling water, but requires 1000 parts of cold water for its solution. Its taste is bitter and astringent. The formula of the crystals is $C_{21}H_{12}O_8+4$ Aq. At 212° it gives off 2 Aq.; it melts at 226°, and boils at 350°, but is decomposed, water being evolved, and a new substance produced. The solution of phloridzine precipitates some metallic salts. The persulphate of iron gives a brown precipitate, but the perchloride of iron produces a blood-red liquor and no precipitate.

The decomposition of phloridzine by heat is not complete until the temperature rises to 450°; it then forms a deep red mass of *Rufin*, the same substance as is produced by the action of oil of vitriol on salicine; it is very soluble in alcohol, insoluble in ether; boiled in water, it dissolves, but loses its red colour, and the liquor, on cooling, becomes milky. It dissolves in water of ammonia or potash with a rich red colour, and is precipitated on the addition of an acid; its formula is $C_{14}H_7O_5$; it combines with oil of vitriol, forming *Rufin-sulphuric Acid*, which unites with the metallic oxides, forming red or brown salts, which possess considerable analogy to the sulphovinates.

When phloridzine is dissolved in dilute sulphuric acid, and the liquor boiled, a white crystalline substance separates, which is termed *Phloretine*; the liquor then contains much grape sugar. The formula of phloretine is $C_{51}H_{26}O_{17}$; its taste is sweet; it is sparingly soluble in water, but very soluble in alcohol; it melts at 300°; when heated with nitric acid, it forms *Phloretic Acid*, the formula of which is $C_{51}H_{24}.N_2O_{35}$; it is a yellow-brown powder, of a velvety aspect, but not crystalline; insoluble in water, and soluble in alcohol.

The most remarkable action on phloridzine is that exercised by ammonia with access of air. Over a capsule containing water of ammonia are arranged several capsules containing phloridzine in very thin layers, and the whole is so covered with a large bell-glass as that the air shall have free access; after a few days the contents of the capsules are changed into a thick sirupy liquor, nearly black; the excess of ammonia being removed by exposure in vacuo with sulphuric acid, the excess of phloridzine is dissolved out by alcohol, and the residue then being dissolved in water, gives a magnificent blue liquor, from which the colouring substance, *Phloridzeïn*, is precipitated by the cautious addition of acetic acid; it is not crystalline; it forms a transparent resinous mass of a rich crimson colour; its taste is bitter; boiling water dissolves enough of it to be coloured red, but cold water, alcohol, or ether appear scarcely to act upon it.

The formula of phloridzeïn is $C_{21}H_{14}.O_{13}N.+$Aq.; it is formed, therefore, by the combination of phloridzine with five atoms of oxygen and one of ammonia; it is not, however, a salt of ammonia, for the alkalies dissolve phloridzeïn without alteration, forming magnificent blue solutions; from metallic solutions it precipitates purple or blue lakes, the composition of which renders it probable that the equivalent of phloridzeïn is $C_{42}H_{28}.O_{26}N_2+2$ Aq.; then the

Phloridzeïnate of ammonia, $=C_{42}H_{28}.N_2O_{26}+N.H_3$.
Phloridzeïnate of silver, $=C_{42}H_{28}.N_2O_{26}+2Ag.O$.
Phloridzeïnate of lead, $=C_{42}H_{28}.N_2O_{26}+2Pb.O$.

If the blue solution of phloridzeïnate of ammonia be put in contact with a slip of zinc, protochloride of tin, sulphuretted hydrogen, or any other deoxidizing agent, it is deprived of colour, but by exposure to the air it rapidly reassumes its tint; with chlorine the colour is instantly and permanently destroyed.

Asparagine. Aspartic Acid.

Asparagine is found in the young shoots of asparagus and of potatoes, in the roots of liquorice and marsh-mallow. From the latter it is easily prepared. The decorticated roots are to be digested in cold water for forty-eight hours, and the liquor then strained and evaporated to the consistence of a sirup. By standing for some time, the asparagine gradually crystallizes, and the crystals are to be purified in the ordinary manner by animal charcoal. It forms rectangular octohedrons and prisms; it is colourless and tasteless; it requires about sixty parts of cold, but much less of hot water for solution; it is insoluble in alcohol; it contains nitrogen, its formula being $N.C_4 . H_4O_3 + Aq.$; the water goes away by a heat of 230°.

When asparagine is boiled with a strong solution of barytes, ammonia is expelled, and aspartate of barytes formed; by cautiously adding sulphuric acid, the barytes may be precipitated, and the liquor yields, on evaporation and cooling, crystallized aspartic acid. In this reaction $2(N.C_4 . H_4O_3)$ produces $N.H_3$ and $N.C_8 . H_5O_6$, which is the formula of aspartic acid. This substance is tasteless, sparingly soluble in cold, but abundantly in boiling water, and is deposited as a white crystal line powder as the solution cools; it reddens litmus. Its salts are generally soluble, except those of lead, silver, and black oxide of mercury.

It is not easy to decide whether the ammonia exists ready formed or not in the asparagine; if so, the remaining organic element may be aconitic acid (see p. 597), and then there should be,

Asparagine=anhydrous aconitate of ammonia$=C_4H.O_3+N.H_3$.
Aspartic acid=anhydrous binaconitate of ammonia$=2(C_4H.O_3)+N.H_3$.

In the case of the anhydrous compounds of ammonia with the mineral acids, it is retained with the same obstinacy as in asparagine (see p. 508).

Caffeïne or Theïne. Caffeïc Acid.

This has been found only in the coffee-berry, the tea-leaf, and the paulinia sorbalis (guaranà). To prepare it, raw coffee is to be boiled in water, and the decoction treated with subacetate of lead as long as the precipitate which forms is coloured. The caffeïne crystallizes from the filtered liquor by evaporation and cooling; if it be coloured, it is to be boiled with oxide of lead and ivory black, and again crystallized; when pure, it forms brilliant long needles of a rich satiny lustre; its taste is purely bitter; it dissolves in fifty parts of cold, but in much less of boiling water; it is very soluble in proof spirit, but insoluble in absolute alcohol; its solutions react neither acid nor alkaline; it is not precipitated by any metallic salt. Caffeïne is remarkable for the large quantity of nitrogen it contains (29 per cent.), being more than any other vegetable substance; its formula is $N_2C_8 . H_5O_2+Aq.$ When caffeïne is boiled with solution of barytes, cyanuric acid, ammonia, formic, and carbonic acids are produced.

The coloured precipitate produced in the decoction of raw coffee by acetate of lead contains two peculiar substances, which may be extracted from it by treatment with a stream of sulphuretted hydrogen gas, evaporation to the consistence of a sirup, and digestion of the residue in strong alcohol. That which dissolves is *Caffetannic Acid;* it is dark brown; tastes acid and astringent; colours the persalts of iron emerald green; it precipitates the salts of barytes and lime yellow, of copper green, but does not affect tartar-emetic. The substance insoluble in alcohol is a white powder, which, when heated, evolves the characteristic aromatic smell of roasted coffee; its solution in water reddens litmus; it is termed *Caffeïc Acid.*

These bodies have not been accurately examined. It is not known if the tannic acid of tea and coffee be the same.

Piperine.—$N.C_{34} . H_{19}O_6$.

This substance exists in white, black, and long pepper; it is prepared from white pepper by digestion in spirit of wine, and distilling the liquor to the consistence of an extract, from which, by digestion in a solution of caustic potash, a quantity of resin is to be removed; the residue is then to be dissolved in alcohol, and the solution abandoned to spontaneous evaporation, when the piperine gradually crystallizes in transparent rhombic prisms. It melts at 212°; is tasteless and inodorous; destitute of either acid or basic properties; nitric acid colours it red; when heated strongly, it yields ammoniacal products.

Cantharidine.—$C_{10}H_6O_4$. This substance is extracted from the blistering fly (various species of cantharis and lytta) by digesting a watery extract of the flies in alcohol, evaporating the solution to dryness, and treating the residue with ether, which dissolves out the cantharidine. By spontaneous evaporation it is obtained crystallized; it forms colourless pearly scales, which fuse when gently heated, and sublime unaltered at a higher temperature; it is, when pure, insoluble in water and in cold alcohol; it is perfectly neutral, and has no affinity either to acids or bases.

Anemonine. Anemonic Acid.

This substance exists in various species of anemone; it is extracted by distilling the plant with water; it separates, after some time, from the distilled water, in brilliant white needles; it melts and volatilizes at a high temperature, yet not without partial decomposition; its formula is $C_6H_3O_4$; when it is dissolved in strong muriatic acid, and the liquor evaporated to dryness, *Anemonic Acid* is formed; its formula is $C_6H_4O_5+Aq$. It is not important.

Cetrarine, or *Lichen Bitter.*

This substance is found in Iceland moss; to extract it, the lichen, being well crushed, is to be digested in alcohol as long as this acquires a bitter taste; the liquor may then be distilled in great part off, and the cetrarine is deposited, on cooling, in granular crystals; these are to be, while still moist, washed with ether and cold alcohol, by which they are rendered white, and then being dissolved in 200 times their weight of boiling alcohol, the pure cetrarine separates on cooling as a white powder of a slightly crystalline aspect. It is but sparingly soluble in any menstruum; its only remarkable character is, that by digestion with muriatic acid it forms a deep blue mass, but the nature of the reaction is not known, as the con stitution of these bodies has not been accurately investigated.

Picrotoxine, or *Cocculine.*

This substance exists in the seeds of the menispermum cocculus (cocculus Indicus), constituting their active ingredient; to prepare it, the seeds, freed from the capsules, are to be digested in alcohol, and the solution evaporated to an extract; this is to be then treated with water as long as anything is dissolved, and then some muriatic acid added to the liquor; by cooling, the cocculine crystallizes in brilliant white needles. Its reaction is neutral; its taste intensely bitter; it dissolves moderately in boiling, but sparingly in cold water. The portion of the alcoholic extract which does not dissolve in water contains another substance, *Picrotoxic Acid,* which is brown, and possesses the properties of a resin; it dissolves in alkaline liquors, from which acids throw it down unchanged. The formula $C_{10}H_6O_4$ has been assigned to picrotoxine, and that of $C_{11}H_6O_4$ to picrotoxic acid.

Columbine.—Found in the roots of the menispermum palmatum. The coarsely-powdered columbo-roots are to be digested in ether, and by the spontaneous evaporation the columbine crystallizes; or by digesting the roots in alcohol, and decolorizing the liquors by animal charcoal, it may also be prepared; it forms brilliant right rhombic prisms; its taste is intensely bitter; its reaction neutral; it dissolves but sparingly in water, alcohol, or ether; its solution does not precipitate any metallic salt; its formula appears to be $C_{24}H_{12}O_7$.

Cusparine.—This is the active principle of the true angustura (cusparia febrifuga). The bark is to be extracted by alcohol, and the solution concentrated very much by spontaneous evaporation; on cooling then below 32°, granular crystalline masses of cusparine separate, from which the liquor is to be strained; by redissolving in alcohol, and precipitation of the colouring matter by acetate of lead, it is ultimately obtained pure. When crystallized from a solution some degrees below 32°, cusparine forms colourless but irregular needles; by a very gentle heat it melts and gives off twenty-three per cent. of water of crystallization; it dissolves readily in water and alcohol, but is insoluble in ether; by heat it is totally decomposed; its solutions precipitate most metallic salts. Its composition is not known.

Elaterine is the active material of the expressed juice of the momordica elaterium; the juice, being evaporated to the consistence of an extract, is to be digested in strong alcohol; the solution thus formed is to be distilled to a small bulk, and then, on being mixed with water, it deposites the elaterine as a white crystalline powder. It melts at about 320°, but is totally decomposed by a stronger heat; its taste is

intensely bitter; it is almost insoluble in water, but abundantly in alcohol; it possesses no characteristic chemical property.

Meconine.—This substance exists mixed with the more important ingredients in opium; it is most abundant in the inferior kinds; its preparation is very circuitous, and will be described in the general analysis of opium, under the head of narceïne. Meconine crystallizes in white six-sided prisms; it melts at 194°, and may be sublimed unaltered; it dissolves sparingly in cold, but moderately in boiling water, abundantly in alcohol and ether; its formula appears to be $C_{20}H_9O_7+Aq$. By nitric acid it is dissolved, and a substance crystallizes from the liquor in long needles, which is termed *Nitromeconic Acid;* its formula is $N.C_{20}.H_9O_{12}$; its solution in water reddens litmus; it volatilizes at 370°, but is partly decomposed. By contact with chlorine, meconine is coloured red, and substances formed whose constitution is not well known.

Peudecanine.—This substance is found in the roots of the peudecanum officinale, and is extracted by digestion with alcohol and evaporation; it crystallizes in delicate white needles of a slightly aromatic taste; it fuses at 140°; it is insoluble in water, and but sparingly in cold alcohol; it dissolves copiously in boiling alcohol, in ether, and the oils.

Æsculine, or *Polychrome.*

A great number of vegetables give, when treated with hot water, a solution which appears yellow by transmitted, but violet or blue by reflected light. This phenomenon results from the presence of a body hence called *Polychrome,* and also *Æsculine,* being most abundant in the bark of the horse-chestnut. The bark is to be digested in alcohol, and the liquor to be concentrated by distillation to the consistence of a sirup, in which, when set aside for some weeks, the æsculine crystallizes; by washing with ice-cold water it is freed from the liquid extractive matter; the impure crystals are to be dissolved in a boiling mixture of five parts of alcohol with one of ether, from which, by cooling, the pure substance separates, perfectly colourless, and generally as a light powder, like magnesia alba. It tastes bitter; it dissolves in 672 parts of water at 50°, and in thirteen parts at 212°; its cold, watery solution is perfectly colourless by transmitted, but slightly blue by reflected light; if spring-water be used, the blue becomes much stronger; acids destroy this property, but it is restored to the solution by the addition of a few drops of any alkali.

The watery solution of æsculine reddens litmus, yet it does not neutralize the alkalies, nor precipitate any of the ordinary metallic salts; it dissolves abundantly in alkaline liquors, and the solutions give a magnificent play of colours with reflected light; its formula is $C_{16}H_9O_{10}$.

Populine exists in the bark and leaves of different species of populus, along with salicine; the latter is removed from the liquors by precipitation with acetate of lead, and then, by evaporation, the populine is obtained crystallized; its taste is bitter-sweet, like liquorice; it is very sparingly soluble in water; when heated, it fuses, and is then decomposed; like salicine, it gives with nitric acid, picric acid, and with sulphuric acid, rutilin; its composition is not known.

Quassine constitutes the bitter principle of the quassia amara and excelsa. The rasped wood is to be boiled several times with water, and the filtered decoction evaporated down to three fourths the weight of the wood employed. The liquid, when cold, is to be mixed with slacked lime, and, after twenty-four hours, filtered and evaporated nearly to dryness; the residue is to be treated with alcohol, and the solution distilled in a water-bath to dryness; it is then impure quassine; it is to be washed with ether, and then redissolved in alcohol, and this treatment repeated until it becomes completely white.

Quassine forms small white prisms of an intense but purely bitter taste; but sparingly soluble in water or in ether, it dissolves abundantly in alcohol; when heated, it fuses like a resin; its solution is not precipitated by any metallic salt, but abundantly by tannic acid; its formula is $C_{20}H_{12}O_6$.

Santonine.—This substance exists in the flowering tops and seeds of a number of species of artemisia, from one of which (art. santonica) it derives its name. To prepare it, four parts of the seeds are to be mixed with one and a half of dry lime, and boiled in twenty parts of alcohol three times; the united decoctions are to be distilled to fifteen parts; the residue, when cold, is to be filtered, evaporated to one half, and, having been rendered slightly acid by vinegar, boiled for some time; on cooling, the santonine crystallizes in large feathery crystals, which are to be purified from an adhering resinous substance by washing with alcohol. Being then re-

dissolved, and the solution slowly cooled, the santonine crystallizes in colourless rectangular prisms and plates; it is tasteless; it is very sparingly soluble in water; more so in alcohol and ether; at 338° it melts, and by a carefully-applied heat may be sublimed without decomposition, otherwise it becomes brown, and a yellow crystalline substance is formed. Santonine appears to possess feeble acid properties; it produces with the alkalies soluble, and with the earths and ordinary metallic oxides insoluble compounds, but they are of instable constitution. The formula of santonine is $C_{10}H_6O_2$.

By exposure to light, santonine undergoes a change apparently isomeric; it becomes gold-coloured, and forms yellow solutions, which, however, soon become colourless.

Saponine.—This substance is most easily extracted from the roots of the saponaria officinalis by boiling in weak spirit; on cooling, the saponine separates; it is purified by digestion with animal charcoal; it is a white powder, of a sharp, piquant taste; very soluble in water, it is sparingly soluble in alcohol, and insoluble in ether; its formula appears to be $C_{26}H_{23}O_{16}$. By the action of nitric acid, saponine forms mucic acid and a resinous substance; when dissolved in solution of caustic potash, it forms *Saponinic Acid*, which is precipitated as a white powder on adding a stronger acid to the liquor. The formula of saponinic acid is $C_{26}H_{22}O_{12}$. It is insoluble in cold, but soluble in boiling water.

Scillitine is the active principle of the squill (scilla maritima). The fresh juice is evaporated, and the extract treated with alcohol. The spirituous solution is to be dried down, and the residue, being dissolved in water, is to be precipitated with acetate of lead, and filtered; sulphuretted hydrogen being passed through the clear liquor removes the excess of lead, and then, by filtration and evaporation, the scillitine may be crystallized.

It forms a hard, brittle mass, like resin, of an intensely bitter taste; it deliquesces and dissolves readily in alcohol and water, but not in ether.

Senegine.—This substance is extracted from the roots of the polygala senega by boiling with water, precipitating the concentrated decoction with the acetate of lead, filtering and removing the excess of lead from the solution by sulphuretted hydrogen, and evaporating cautiously to dryness; the residue is to be digested in alcohol, and this solution being dried down, the product is to be digested in ether. The material which remains undissolved is then to be passed through the same series of operations until it becomes a white pulverulent mass, which is pure *Senegine*. It is sparingly soluble in cold, but abundantly in boiling water; it is very soluble in alcohol, but insoluble in ether. With sulphuric acid it produces a curious play of colours, becoming first yellow, after some time rose-red, and then dissolving; the solution gradually becomes violet, after some time grayish-blue, and finally colourless, while a gray precipitate falls down. Senegine appears to possess feeble acid properties.

Smilacine, or *Sarsaparilline.*—This substance is found in the roots of the smilax sarsaparilla and the bark of the China nova. It is obtained by boiling with alcohol, and distilling the decoction to two thirds; on cooling, the smilacine crystallizes, and is purified by animal charcoal and recrystallization. It is white, in very minute needles; its taste nauseous and slightly bitter; very sparingly soluble in water, more so in alcohol, most in ether; with sulphuric acid it gives colours like those of senegine.

Absinthiïne.—The bitter principle of the wormwood (artemisia absinthium). It is prepared by a succession of operations almost identical with those described for obtaining senegine; it is hence unnecessary to repeat their description. When completely pure, it is white and crystalline; its taste is intensely bitter; it fuses at a high temperature, and closely resembles a resin; its best solvent is alcohol. It possesses the characters of a weak acid, being much more soluble in alkaline liquors than in pure water, and being precipitated from such solutions on the addition of an acid. With oil of vitriol, it is coloured first yellow, and then dark reddish purple.

Lactucine is obtained by digesting the inspissated juice of the lactuca virosa (lactucarium) in ether; by the spontaneous evaporation of the solution, it forms a mass of crystalline needles, slightly coloured yellow; it has a strong bitter taste, is fusible, and may be partly volatilized; it is soluble in water, alcohol, and ether. It is decomposed by strong acids, and appears not to have any tendency to form salts.

Of Extractive Matter. Apotheme. Extracts.

If from any plant, or portion of a plant, the soluble ingredients be dissolved out by water, a variety of substances exist in the liquor, some acid, others basic, others indifferent; of these bodies, the majority possess the property of absorbing oxygen when the solution is exposed to the air, and often, also, of evolving carbonic acid, changing thereby into substances insoluble, or scarcely soluble in water. Thus gallo-tannic acid first forms gallic acid, and is then converted into a brown insoluble mass; so gum and sugar ultimately produce certain forms of ulmine; and there are few of the neutral principles described in the present chapter that do not rapidly undergo a similar change.

During the evaporation of a vegetable infusion or decoction, these reactions rapidly occur, being promoted by the heat; the liquor, which had been at first clear, becomes turbid and brown, a deposite forms, and when, finally, it has been evaporated to the consistence of a thick sirup, what remains is termed an *extract;* it is a mixture of the constituents of the plant in great part decomposed. If this extract be treated with water, and the soluble portion again evaporated, the same changes occur, so that, no matter what may have been the original nature of the vegetable substances, they are ultimately reduced to this insoluble and inert condition. This brown substance is termed *Apotheme;* its true nature is not known, but it is probable that its composition and properties vary in some degree with the nature of the substance it is formed from; we do not even know of its relations to the various kinds of ulmine; though, from its solubility in alkaline liquors, and its precipitating metallic salts, its being separated from these by acids, and obstinately retaining a portion of the acid used to precipitate it, its identity with ulmic acid or humic acid is not improbable.

When the conversion of the real constituents of the plant into apotheme is yet incomplete, the material, which dissolves equally in water and dilute alcohol, but not in absolute alcohol or in ether, is termed *extractive.* Such a mixture can have no distinctive chemical properties; it is more or less coloured, and uncrystallizable; it precipitates metallic salts; it absorbs oxygen, forming apotheme (oxidized extractive). The different classes of plants are considered by pharmaceutic writers to contain different kinds of extractive matter; there are thus *bitter extractive, gummy extractive, astringent extractive,* and so on; but, to the chemist, these names convey only the idea of absolute ignorance of the real nature of these bodies; the chemist recognises no such substance as *extractive matter,* or *Apotheme;* they are merely complex products of decomposition of other bodies, and have not, as yet, been accurately examined. In the preparation of an extract of a plant, the ambition of the operator should be, not to have either extractive or apotheme produced, but, by employing the lowest possible temperature, and excluding air as much as possible, to obtain the constituents of the plant in a concentrated form, but not destroyed, as they too frequently are, by the operation: accordingly, in the manufacturing laboratory of the Apothecaries' Hall of Ireland, the greatest precautions are taken to ensure success in the preparation of extracts; but details of the methods belong to pure pharmacy, and are unfitted for the present work.

A great number of bodies, that have been from time to time announced as the active principles of many plants containing them, are really but such extracts, prop-

erly prepared, but still not the pure chemical substances. Thus, from colocynth, *Colocynthine;* from hippo, *Emetine;* from rhubarb, *Rheïne*, &c. It is on this account that many bodies, to which distinct names have been given by their discoverers, as chemical species, are not noticed as such by me.

The *bitter principle of the Aloës* is one of these which have never been obtained chemically pure, and yet the very remarkable products of the action of nitric acid on it show that it is a truly distinct substance. When socotrine or hepatic aloës are digested with hot nitric acid, red fumes are abundantly evolved, and four different acids produced, for the accurate examination of which we are indebted to Schunk. They are, the *Aloëtic Acid*, the *Aloë-resinic Acid*, the *Chrysammic Acid*, and the *Chrysolepic Acid*, and they are generated by successive oxidation of the bitter principle of the aloës, in the order in which their names stand.

The *Aloëtic Acid* is a yellow powder, insoluble in water, but forming soluble salts, of which that with potash crystallizes in ruby-red needles. The *Aloë-resinic Acid* is soluble in water; its potash salt uncrystallizable; its combinations with the metallic oxides insoluble, and generally brownish-red. The analyses of these bodies are not yet published.

The *Chrysammic Acid* is a greenish-yellow crystalline powder; it is very sparingly soluble in water, yet tinges it purplish-red; it is more soluble in alcohol, ether, and acids; when heated, it fuses, and is then decomposed with a slight explosion, and a bright but smoky flame; it contains nitrogen; its formula is $C_{15}H_2 . N_2O_{12}+Aq$. The chrysammate of barytes is a red insoluble powder. The chrysammate of potash is the most insoluble of all the salts of potash, requiring 1250 parts of water at 60° for solution, and may hence serve as an excellent reagent for that alkali; it is a dark red crystalline powder when precipitated, but when it crystallizes from a hot dilute solution, it forms gold-coloured plates.

The *Chrysolepic Acid* is distinguished by its solubility in water; it crystallizes in beautiful gold-coloured plates, closely resembling *Picric Acid*, with which it is isomeric, its formula being $C_{12}H_2 . N_3O_{13}+Aq$. It is distinguished, however, by the much greater solubility of its potash salt, and by the action of heat, as it may be fused and volatilized without decomposition, if cautiously heated.

CHAPTER XXVI.

OF THE COLOURING MATTERS.

THE substances to be now described may be arranged in two classes, according as they pre-exist in the plant, or as they are merely products of the decomposition of other bodies which are not coloured; of these last an example has already been given in the formation of phloridzeïne from phloridzine.

SECTION I.

OF THE PRE-EXISTING COLOURING MATTERS.

Colouring Principles of Madder.

The dried roots of the rubia tinctorum constitute the madder of commerce, which, furnishing the well-known Turkey red, is perhaps the most important of the dyestuffs. The constitution of madder is very complex; it contains five different colouring matters and two colourless acids, the general preparation and properties of which are as follows:

Madder Purple, or *Purpurine.*—Madder roots are to be well washed with water at 80°, then boiled several times in a strong solution of alum, and each liquor filtered while very hot. On cooling, a red-brown substance precipitates, which is impure *Madder Red;* it is to be separated

by the filter. On adding to the clear red solution some sulphuric acid, the madder purple is thrown down. To obtain it quite pure, it is to be dissolved in boiling alcohol, and the solution allowed to evaporate slowly. It separates as a fine orange-red crystalline powder, sparingly soluble in cold, but more easily in boiling water. The solution is rose-red; its solutions in ether and alcohol are bright red. Acids turn it yellow; alkalies dissolve it with a rich red colour. It is fusible, and, when more strongly heated, a portion sublimes as a red powder, but the greater part is decomposed.

Madder Red, or *Alizarine,* as precipitated in the preparation of purpurine, is to be purified by repeated boiling with solution of alum, and then crystallized by solution in ether and spontaneous evaporation. It is a brownish-yellow crystalline powder. When heated, it sublimes, forming brilliant orange needles; it is sparingly soluble in water, more so in alcohol and ether. Ammonia dissolves it with a purple red, and potash or lime with a violet colour. The formula $C_{37}H_{12}O_{10}$ has been assigned to this body.

Madder Orange.—The roots are to be digested for sixteen hours in eight parts of water at 70°; the infusion is to be filtered and set aside; small orange crystals gradually form; these are to be collected and dissolved in boiling alcohol. On cooling, the madder-orange crystallizes as a yellow powder. When heated, it fuses, and is decomposed in great part, some of it subliming in yellow fumes; it is most easily soluble in ether; it dissolves in alkaline, forming brown-red liquors.

Madder Yellow, or *Xanthin.*—The cold infusion of madder is to be mixed with an equal volume of lime water. The dark-red precipitate is to be treated with dilute acetic acid; the lime and the yellow dissolve; any traces of the other colouring matters are removed from the liquor by a woollen cloth mordanted with alum. The solution is to be then evaporated, the residue dissolved in alcohol, and precipitated by sugar of lead; the scarlet precipitate separated, and decomposed by sulphuretted hydrogen. The liquor so obtained gives, on evaporation, the xanthine pure; it is yellow, uncrystallizable, and very soluble in alcohol and water.

Madder Brown is totally insoluble both in alcohol and water. The acids which exist in madder are but very little known, and do not possess any interest either technical or scientific.

Of these colouring matters, the *Red,* or *Alizarine,* is the most important, as it forms with an alumina mordant the magnificent *Turkey Red.* With an iron mordant it gives a permanent black, and with mixed mordants of the two, various intermediate shades of purple. The great complexity of the process for dyeing Turkey red arises from the difficulty of dissolving away the other four bodies, so that only pure madder red may remain.

Alkanna Red, or *Anchusic Acid.*

This substance exists in the roots of the anchusa tinctoria. They are to be well boiled in water, and then digested in a solution of carbonate of potash; on the addition of an acid to this liquor, the colouring matter precipitates; it may also be obtained by digesting the roots in alcohol and evaporating; it is a dark-red resinous body, insoluble in water, soluble in alcohol, ether, and the essential oils; it combines with alkalies, forming blue solutions, which give blue or crimson lakes with metallic salts. The formula $C_{17}H_{10}O_4$ has been assigned to this body.

Braziline is the colouring matter of various species of cæsalpina (Brazil wood,

fernambouc wood). The decoction of the wood in water is to be agitated with hydrated oxide of lead, then filtered and evaporated to dryness. The residue is to be treated with alcohol, the solution mixed with water and gelatine, which throws down a quantity of tannic acid, then filtered, again dried, mixed with alcohol, and filtered to separate the excess of gelatine, then again evaporated, and set aside to crystallize.

When pure, braziliïne forms orange crystals; it is soluble in water, alcohol, and ether; the solutions are reddish-yellow; alkalies and most metallic salts give purple, and alum a red precipitate, with the solution of braziliïne

Santaline exists in the red sanders wood (pterocarpus santalinus). Its extraction and properties are exactly similar to that of the *Alcanna Red.* Its formula is $C_{16}H_8O_3$.

Hæmatoxyline.—This substance, the colouring principle of the logwood (hæmatoxylon Campechianum), is frequently met with naturally crystallized in stellated groups of prisms, sometimes of considerable size, in clefts of the wood; it may also be prepared by a process similar to that described for braziliïne; it is slightly bitter and astringent; it is very sparingly soluble in water, but copiously in alcohol and ether, forming brownish-red liquids. Acids colour its solutions yellow, alkalies purple; with the earths and metallic oxides it forms purple or blue lakes.

Safflower Red, or *Carthamine.*

The petals of the safflower (carthamus tinctorius) contain a red and a yellow material; the former alone is of technical importance. The flowers are to be washed with water acidulated with acetic acid until all the *Safflower Yellow* is removed. By digestion then in a solution of carbonate of soda, the carthamine is dissolved, and may be precipitated by any acid, but citric acid answers best; it forms a dark red powder, insoluble in water and in acids, and but sparingly soluble in alcohol or ether; it reddens litmus, and gives with the alkalies yellow solutions; its compound with soda crystallizes in silky needles; with alumina it forms a beautiful red lake, *Rouge,* used as a cosmetic and in dyeing. This substance is much employed for dyeing silk of various shades of pink and rose colour.

I have found in the petals of the salvia fulgens a colouring matter possessing considerable analogy to carthamine, and capable of being substituted for it.

Quercitrine.—This substance is extracted from the bark of the quercus infectoria by simple decoction in water; after some days the colouring matter separates in crystals; or, better, by digesting the bark in alcohol, precipitating the tannin by gelatine and evaporation: when pure, it resembles very minute crystals of yellow prussiate of potash; it is easily soluble in water and in alcohol, and appears to possess feeble acid properties. Its formula, by Bolley's analysis, appears to be $C_{16}H_9O_9$ $+$Aq. With metallic oxides it gives brilliant yellow lakes.

Chrysorhamnine. Xanthorhamnine.

I have found the unripe berries of the rhamnus tinctorius (Persian berries, grains d'Avignon) to contain a substance soluble in alcohol and ether, and crystallizing from its ethereal solution in minute silky needles of a brilliant yellow colour; it gives with metallic oxides yellow lakes. When cautiously heated it fuses, but is not volatile. In the ripe berry, this substance, to which I have given the name *Chrysorhamnine,* is totally replaced by another, which I term *Xanthorhamnine,* which is of a much less beautiful yellow, and does not crystallize; this change is effected, also, by boiling the chrysorhamnine for a few minutes with water, or by contact with alkalies. The xanthorhamnine is totally insoluble in ether, but easily soluble in alcohol and water. It is formed by the union of the elements of water with chrysorhamnine. Its silver salt is yellow when first thrown down, but rapidly becomes black, metallic silver separating, and a colourless organic substance being formed. The Persian berries are much used for dyeing yellow, but, from the processes employed, the xanthorhamnine alone is actually brought into play.

Luteoline is the colouring principle of the weld (reseda luteola), and probably of the dyers' broom (genista tinctoria). Its mode of preparation resembles that of quercitrine. It is soluble in water, alcohol, and ether; it combines with both acids and alkalies, forming yellow compounds. With alumina and the oxides of tin and lead, it gives brilliant yellow lakes; with iron, a dark brown precipitate.

Morine is the colouring principle of the yellow-wood (morus tinctorius); it is prepared like quercitrine, with which its properties accurately agree.

Orelline.—The seed of the bixa orellana are imbedded in an orange-red colouring

matter, which is separated by washings and a kind of fermentation; when deposited from the liquors, so as to form a consistent paste, it is sent into commerce under the names of *Rocou*, *Orleans*, or *Anotta*. To obtain the colouring principle pure, the orange-red mass is digested in alcohol, and the solution distilled nearly to dryness; the residue is then treated with ether, which dissolves the orelline, and yields it, on evaporation, as an orange-red, somewhat crystalline powder; it colours water pale yellow; it is more soluble in alcohol, but gives with ether or oils deep red solutions; it dissolves in alkalies, and is precipitated therefrom by acids. With alumina, oxide of tin, and oxide of lead, it gives fiery red precipitates. It is extensively used in dyeing, and also to heighten the colour of cheese and butter.

Curcumine is found in the roots of the curcuma longa (turmeric), and is obtained by treatment with boiling alcohol, evaporation to dryness, and digestion of the residue in ether, which dissolves the pure colouring matter, and yields it by spontaneous evaporation. Curcumine melts at 104°; it possesses the properties of a resin; alkalies brown it, on which its employment for a test-paper rests; acids render its proper yellow much paler, except boracic acid, which stains it yellowish-red.

Berberine exists in the roots of the berberis vulgaris; it is prepared by boiling the roots in water, and evaporating the decoction to the consistence of an extract, which is to be treated with spirit of wine as long as this acquires a bitter taste. The spirit is to be distilled in great part off, and the residue suffered to stand in a cool place for twenty-four hours; the crystals which form are to be recrystallized, first from water, and then from alcohol. Pure berberine forms a light crystalline yellow powder of a strongly bitter taste; it is very sparingly soluble in cold, but abundantly in boiling water and in alcohol; it is insoluble in ether. At 268° it melts, and, if farther heated, is decomposed, giving ammoniacal products; by chlorine it is converted into a brown-red substance; it combines with bases, acting feebly as an acid; its alkaline compounds crystallize; those with the earths and heavy metallic oxides are insoluble, and generally yellow; a solution of it precipitates the iodide, cyanide, ferrocyanide, and sulphocyanide of potassium. Berberine contains nitrogen, its formula being $N.C_{33} . H_{18}O_{12}$.

Cochineal Red, or Carmine.

This very remarkable substance differs from all of the other colouring matters here described, in being a product of the animal kingdom. It exists in many insects of the genus coccus, as the coccus cacti (the true cochineal), the coccus ilicis (kermes), the coccus ficus (lac dye), &c. For its preparation the cochineal is to be digested in ether to remove a quantity of fat, and then boiled in alcohol as long as this is coloured. The alcoholic liquors, being mixed, are to be concentrated by distillation, and then cautiously dried; the impure carmine thus obtained is digested in alcohol, and the solution mixed with ether, which precipitates the colouring matter quite pure.

It is a purple red powder, easily soluble in water and alcohol, insoluble in ether. It melts at 122°, but is decomposed by a high heat; chlorine turns it yellow; alkalies colour cold solution of carmine red, but it becomes yellow by exposure to the air or by boiling. With alumina it forms a precipitate, which is crimson when prepared with a cold, but violet if with a hot solution. All metallic salts give lakes with the alkaline solution of carmine; that of the protoxide of tin is a rich scarlet. The carmine of commerce is an alumina lake more or less pure; that called *Chinese Carmine* is the compound with oxide of tin.

The carmine contains nitrogen; the formula $N.C_{32} . H_{26}O_{20}$ has been assigned to it, but cannot be considered as definitely established.

Of Indigo, and the Bodies derived from it.

The blue indigo of commerce is derived from the leaves of a variety of plants of different genera. The genus indigofera includes a number of productive species, also the genera nerium and isatis, marsdenia, asclepias, and polygonum, galega, spilanthus, and amorpha. Of these the great majority are natives of the tropics; but a few, as the isatis tinctoria, and the polygonum tinctorium, belong to temperate regions, the former being indigenous both to Ireland and to England.

The indigo is secreted in the cellular tissue of the leaf, in a form (white

indigo) which can also be artificially produced; it is then colourless, and remains so as long as the tissue of the leaf is perfect. When the leaf begins to wither, oxygen is absorbed, and, the indigo assuming its colour, the leaves become covered with a number of blue points, the first appearance of which shows that the period for collecting them has arrived. The fresh leaves are thrown into large vats with some water, and pressed down by weights. After some time, a kind of mucous fermentation sets in, carbonic acid, ammonia, and hydrogen gases are evolved, and a yellow liquor is obtained, which holds all the indigo dissolved. This is separated, mixed with lime-water, and then exposed to the air until the indigo becomes blue and insoluble, and is completely deposited as a precipitate. The theory of this action is, that, by the putrefaction of the vegeto-animal matter of the leaves, the indigo is kept in the same white, soluble condition in which it exists in the plant, and a clear solution of it being thus obtained, it is precipitated, according as it absorbs oxygen, in a much purer form than otherwise could be effected.

The putrefying pasty mass of leaves obtained from the isatis tinctoria constitutes the *woad* or *wad* employed in the hot indigo bath for dyeing cloth.

The blue indigo, as thus obtained, is still a mixture of several bodies, as indigo-red, indigo-brown, indigo-gluten, which are removed by repeated treatment with alcohol and dilute acids and alkalies. When pure, the precipitated indigo is a rich blue powder, which, when rubbed by a knife, assumes the colour of metallic copper; it is perfectly insoluble; when cautiously heated, it sublimes in rectangular prisms of a dark purple colour and metallic lustre; its vapour is of a rich purple; it contains nitrogen, its formula, as fully established by Dumas, being $N.C_{16}.H_5O_2$.

White Indigo.—When indigo is acted upon by deoxidizing agents, as protochloride of tin, protoxide of iron, or sulphurous acid, it loses its blue colour, and the white indigo, which is insoluble in water, but soluble in alkaline solutions, is produced. Its mode of preparation is simple: one and a half parts of commercial indigo, two and a half parts of slacked lime, and two parts of green copperas, are to be well mixed up with sixty parts of water, in a vessel from which the air is carefully excluded. The protoxide of iron, formed by the action of the lime on the copperas, peroxidizes itself at the expense of the indigo and water, and the white indigo thus formed dissolves in combination with lime. On adding muriatic acid to the clear solution, the white indigo precipitates, and may be obtained dry, as a crystalline powder, by suitable precautions to prevent the access of air.

The simplest theory of this process should be, that the oxide of iron directly abstracted oxygen from the indigo: hence the names of *Deoxidized Indigo* and *Indigogene* were given to the white substance; but the analyses of Dumas have proved that the white indigo is a compound of hydrogen with the blue indigo, its formula being $C_{16}H_5 . N.O_2+H$. In its formation, therefore, water is decomposed, the elements of it combining respectively with the blue indigo and the deoxidizing body.

On the properties of this white indigo depend the important application of indigo as a dyeing material. The indigo is rendered soluble either by lime and copperas (cold indigo bath), or, being diffused through warm water with a quantity of woad, by the fermentation of which ammonia and hydrogen are evolved, a soluble compound of ammonia and white indigo

is obtained (hot indigo bath); the former is employed for cotton, and the latter for woollen cloth. The cloth is immersed in the bath until it has fully imbibed the solution; it is then exposed to the air, the oxygen of which carries off the hydrogen of the white indigo, and the blue insoluble indigo attaches itself to the fibres of the cloth so firmly at the moment of its formation, as to constitute the most permanent and the most beautiful of our blue dyes.

Sulphate of Indigo.—When blue indigo, in very fine powder, is digested with strong oil of vitriol, for which purpose the German or fuming sulphuric acid answers best, it dissolves in great part, and two acids are formed, the *Sulphopurpuric* and *Sulphindylic;* the former is the principal product when the indigo is in excess, the latter when the oil of vitriol preponderates; they are separated by dilution with water, the sulphopurpuric acid being insoluble, while the sulphindylic acid dissolves.

The sulphopurpuric acid, though insoluble in dilute acids, dissolves readily in pure water; it forms, with the alkalies and earths, blue compounds, which are sparingly soluble in water, but soluble in alcohol. By the analysis of Dumas, it appears to consist of $C_{32}H_{10} . N_2O_4 + 2S.O_3$, and in its potash salt to contain one atom of alkali.

The sulphindylic acid, $C_{16}H_5 . N.O_2 + 2S.O_3$, when dried from its solution in water, forms a dark blue mass. Its salts are of a rich blue colour; those of the alkalies are soluble, those of the earths and metallic oxides insoluble in water. They consist, according to Dumas's analysis, of an atom of indigo, two of sulphuric acid, and one of base. The sulphopurpuric and sulphindylic acids thus contain the same organic element (indigo), but in different proportions, united to sulphuric acid.

Berzelius considers that, besides these two, there are generated, by the action of sulphuric acid on indigo, several other acids of complex nature; but, as we possess no exact results concerning them, and as they are of no technical importance, it is unnecessary to describe them in detail.

This solution of indigo in oil of vitriol constitutes the *Saxon Blue,* or *Chemic Blue,* used extensively in dyeing; on neutralizing the liquor by an alkali (carbonate of soda), and immersing the tissue, whether wool, silk, or cotton, the indigo combines with the fibre of the cloth, and the sulphuric acid remains combined with the alkali.

By the gradual oxidation of indigo, a substance is formed which crystallizes in large red prisms, and is termed by Laurent *Isatine;* its formula is $C_{16}H_5 . N.O_4$. If the process be more violently carried on, the constitution of the indigo is broken up, and a new type formed, thus: by the action of an excess of nitric acid on indigo, two remarkable bodies are formed, the *Anilic* and the *Picric Acids.* A mixture of one part of fuming nitric acid and ten of water being brought to boil, indigo is to be added in fine powder as long as any effervescence occurs; the liquor is to be then filtered while hot. Both acids crystallize on cooling; the crystals are to be drained, redissolved in water, and precipitated by acetate of lead; picrate of lead falls; anilate of lead remains dissolved, and, being decomposed by sulphuretted hydrogen, the *Anilic Acid* crystallizes in white needles; its taste is bitter and acid; it requires 1000 parts of cold, and but ten of boiling water; its salts are all soluble; its formula is $C_{14}H_4 . N.O_9 + Aq$.

The *Picric Acid* may be obtained by diffusing the picrate of lead through boiling water, and decomposing it by sulphuretted hydrogen gas; on filtering and cooling, the picric acid crystallizes. It may be obtained, however, much purer and more abundantly by digesting salicine in nitric acid (p. 606), and directly from the substance which exists in coal gas naptha, termed by Laurent hydrate of phenyl; it forms yellow prisms, sparingly soluble in cold water; when heated, it explodes, as do also its salts; its potash salt requires 260 parts of cold water for solution, and it is hence sometimes used as a reagent for that alkali; its formula is $C_{12}H_3 . N_3O_{13} + Aq$.

When indigo is mixed with a strong boiling solution of caustic potash, it dissolves, and *Chrysanilic Acid* is formed, which may be precipitated by muriatic acid as an orange-red powder; it dissolves in alcohol and ether, and crystallizes by the evaporation of the solutions; its formula appears to be $C_{28}H_{10} . N.O_5+Aq$. By exposure to the air while hot, or directly by contact with peroxide of manganese, this acid is converted into another, *Anthranilic Acid*, the properties of which are remarkable; it is soluble, crystallizes, gives very well-marked and crystallizable salts, fuses at 275°, and sublimes a little above that temperature unchanged; if it be strongly heated, however, it is decomposed, the sole products being carbonic acid and a volatile liquid, *Anilene*. The formula of the hydrated anthranilic acid is $C_{14}H_7 . N.O_4$, and it gives $2C.O_2$ and $C_{12}H_7N$.

This liquid, anilene, is a body closely analogous to the melamine (p. 526); it acts as a powerful base, combining with the hydracids directly, and with the oxacids by including an atom of water; it thus resembles ammonia. These important substances, for whose discovery we are indebted to Fritzche, are still under examination.

Action of Chlorine on Indigo.—This subject, so important in relation to the theory of the bleaching of colouring matters, has been very minutely investigated by Erdman, of whose numerous and complex results the elementary nature of this work will allow but a general notice to be given. Dry chlorine has no action on indigo, but in presence of water it converts it into a yellow mass, from which is separated, by distillation, a substance termed *Chlorindopten*, which sublimes in white scales and needles; its formula is $C_{16}H_4 . O_2Cl_4$; it is sparingly soluble in water, copiously in alcohol and ether. This appears to be a secondary product. The substance which remains behind in the retort, on being dissolved in boiling alcohol, yields, on cooling, red prismatic crystals of *Chlorisatine:* its formula is $C_{16}H_4Cl. . N.O_3$; it is hence indigo, in which an equivalent of hydrogen is replaced by chlorine, and united to an atom of oxygen; with an excess of chlorine it gives *Bichlorisatine*, which consists of $C_{16}H_4Cl_2 . N.O_3$. If these bodies be treated with sulphuretted hydrogen, sulphur is set free, and the hydrogen enters into combination; in contact with potash, the elements of an atom of water are assimilated, and an acid formed, which unites with the potash. In this way chlorisatine gives *Chlorisatyd*, $C_{16}H_5Cl. . N.O_3$, and *Chlorisatic Acid*, $C_{16}H_5Cl. . N.O_4$, and bichlorisatine gives two corresponding bodies.

If chlorisatyd be heated, it produces water, chlorisatine, and a violet powder, *Chlorindine*, which has the formula $C_{16}H_5Cl. . N.O_2$, and is hence a compound of indigo-blue with chlorine. By heating bichlorisatyd, the *Bichlorindine*, $C_{16}H_5N. . O_2Cl_2$, is similarly formed.

By passing chlorine through a solution of chlorisatine in alcohol, all hydrogen is removed, and a substance formed which crystallizes in pale yellow plates, and has the formula $C_6O_2Cl_2$; it is termed *Chloranil*. By the secondary reactions of these bodies, a number of others are generated, which it is not necessary specially to describe.

Notwithstanding the attention devoted by the most distinguished chemists to the compounds and derivatives of indigo, the theory of that body remains very obscure. The derivation of picric acid from the body $C_{12}H_5O.+Aq.$ (*Hydrate of Phænyl*), discovered as a product of destructive distillation by Laurent, may serve as a connecting point for many of the bodies derived from indigo, and which otherwise had appeared totally unconnected. Thus the picric acid is evidently formed by the substitution of $3N.O_4$ for $3H.$ in $C_{12}H_5O.$, and the anilene is probably $C_{12}H_5+N.H_2$; other speculative ideas might be brought forward, but I shall only mention that the blue indigo contains exactly the elements of cyanogen and benzyl, $C_2N.+C_{14}H_5O_2$, and that, as the cyanogen is converted so easily into oxalic acid and ammonia, the derived bodies, which contain C_{14}, may thus have their origin.

Of the Colouring Matters derived from the Lichens.

Many species of lichen contain substances which, although colourless themselves, produce, by contact with air and ammonia, the rich purple or blue colouring matters constituting the archil and litmus of commerce. The species of lichen that have been in this respect most accurately examined are the variolaria dealbata by Robiquet and Dumas, and the rocella tinctoria by myself.

The useful substance in the variolaria is termed *Orcine;* it is obtained by digesting the lichen in alcohol, evaporating to dryness, dissolving the extract in water, concentrating the solution to the thickness of a sirup, and setting it aside to crys-

tallize; it forms, when quite pure, colourless prisms of a nauseous-sweet taste; it fuses easily, and may be sublimed unaltered; its formula is $C_{18}H_7O_3+2$ Aq. when sublimed; when crystallized from its aqueous solution, it contains 5 Aq.

If orcine be exposed to the combined action of air and ammonia, exactly as described for phloridzine (p. 607), it is converted into a crimson powder, *Orceïne*, which is the most important ingredient in the archil of commerce. The orceïne may also be obtained by digesting dried archil in strong alcohol, evaporating the solution in a water-bath to dryness, and treating it with ether as long as anything is dissolved; it remains as a dark blood-red powder, being sparingly soluble in water or ether, but abundantly in alcohol; its formula is $C_{18}H_{10}.N.O_8$. The orceïne in archil is, however, frequently found to contain less oxygen, and to be represented by the formula $C_{18}H_{10}.N.O_5$. I have termed the first kind *Alpha-orceïne*, and the second *Beta-orceïne*; in properties they are identical.

Orceïne dissolves in alkaline liquors, with a magnificent purple colour; with metallic oxides it forms lakes, also, of rich purple, of various shades. In contact with deoxidizing agents it combines with hydrogen, as indigo does, and forms *Leucorceïne*, $C_{18}H_{10}.N.O_8+H$. When bleached by chlorine, a yellow substance is formed, *Chlororceïne*, the formula of which I have found to be $C_{18}H_{10}.N.O_8+Cl.$, analogous to the other.

In the rocella tinctoria there is no orcine; the origin of the coloured substances is a body which I have termed *Erythryline;* it is soluble in ether and alcohol, insoluble in water, but is gradually decomposed by it; its formula is $C_{22}H_{16}O_6$. By the action of the air it is gradually changed into *Erythrine*, a substance which dissolves sparingly in cold, but abundantly in boiling water, from which it separates on cooling in brilliant micaceous plates; it is very soluble in alcohol and ether; its formula is $C_{22}H_{13}O_9$. By prolonged boiling in water, erythrine is changed into a substance very soluble in water and in alcohol, *Amarythrine*, the formula of which is $C_{22}H_{13}O_{14}$; and, finally, by the still farther action of the air, *Telerythrine* is formed, which crystallizes in small grains, and has the formula $C_{22}H_9O_{18}$.

If, however, in addition to the air, ammonia have access to these bodies, the crimson colour is produced, and the two varieties of orceïne are formed. I conceive the oxidizing stage to proceed as far as amarythrine, and that, by combination with ammonia and oxygen, a substance is formed, to which I have given the name of *Azoerythrine*. Its formula is $C_{22}H_{16}.N.O_{19}+3$ Aq. By the loss of $4C.O_2$ and $6H.O.$, it gives alpha-orceïne, $C_{18}H_{10}.N.O_5$, which, absorbing oxygen, gradually forms the true or beta-orceïne, $C_{18}H_{10}.N.O_8$.

When an alkaline solution of orceïne is exposed to the air, it absorbs more oxygen, and a substance is produced which constitutes a great part of the colouring material of litmus. I have termed it *Azolitmine;* its formula is $C_{18}H_{10}.N.O_{10}$; it is a dark red powder, which is insoluble in alcohol or ether, and but sparingly soluble in water; it dissolves better in acid liquors, which render it a pale red, and with alkalies it gives the rich blue colour of litmus. With the earths and metallic oxides it forms purple or blue lakes; with deoxidizing agents it is decolorized, forming *Leucolitmine*, and by chlorine a yellow substance is produced, having the formula $C_{18}H_{10}.N.O_{10}+Cl$.

Besides the bodies of the erythrine series, the lichen rocella contains a substance, termed *Rocelline*, which is white, fusible, insoluble in water, soluble in alcohol and ether; its formula is $C_{26}H_{24}O_6$. By exposure to the air, it is converted into a fatty substance of a rich crimson colour, which I have termed *Erythroleïc Acid;* this body exists in archil, and is separated from the orceïne by means of its solubility in ether. Its formula is $C_{26}H_{22}O_8$; it is capable, under circumstances which are not yet well understood, of being broken up into two substances, which are both found to exist in litmus; they are *Erythroleine*, which has the formula $C_{26}H_{22}O_4$, and *Erythrolitmine*, which consists of $C_{26}H_{22}O_{12}$. The erythroleine and erythroleïc acid are, like the alpha and beta orceïnes, distinguished only by their composition; they have the same colour, are sparingly soluble in water, but copiously in alcohol and ether; they dissolve in alkaline liquors with a rich crimson colour, and give crimson lakes with the metallic salts. The erythrolitmine, on the other hand, is bright red, very sparingly soluble in water or ether, but soluble in alcohol. Alkalies turn it bright blue; in a solution of potash it dissolves, but its compound with ammonia is insoluble, and consists of $C_{26}H_{22}O_{12}+N.H_4O$.

The brief history of these substances now given will render intelligible the process of manufacture of archil and litmus, and the principles of their use in the arts and in the laboratory. The lichens employed are ground up with water to a uniform

pulp, and this is then mixed with as much water as makes the whole thick-fluid. Ammoniacal liquors from the gas or ivory-black works, or even stale urine, are from time to time added, and the mass frequently stirred, so as to promote the action of the air. The orcine or erythrine which existed in the lichen absorbs oxygen and ammonia, and forms orceïne; the rocelline absorbs oxygen, and forms erythroleic acid; these being kept in solution by the excess of ammonia, the whole liquid is of an intensely rich purple tint, and constitutes ordinary *archil.* If the oxidizing action of the air be allowed to go too far, we have the purple colour replaced by a shade more or less blue; the orceïne changes to azolitmine, and the erythroleine gives erythrolitmine; a quantity of chalk and plaster of Paris is then added to the liquor, so as to form a consistent paste, and this, cut into little cubical masses and dried, forms the *Litmus* of commerce. From the constitution of archil and litmus, such must be the general principles of the manufacture, although, particularly for litmus, the details are kept very secret by those engaged in the trade.

The use of litmus paper as a test for the presence of a free acid arises from the blue colour belonging to compounds of the erythrolitmine and azoerythrine with an alkali, and as this is taken by even the weakest acid, the red colouring materials are set free.

Of the Colouring Matters of Leaves and Flowers.

The green colour of plants is due to the presence of a substance termed *Chlorophyll.* Even deeply-coloured plants contain but very little of it, and it has not, as yet, been obtained in a state of such purity as that any formula can be assigned to it. It does not contain nitrogen; it is insoluble in water, soluble in alcohol and ether; it is dissolved by strong acids, and precipitated therefrom by dilution; it enters into union with bases, and gives pale green lakes. With deoxidizing agents it shows the same process of decoloration as most other bodies of this class.

Berzelius has noticed that there are really three kinds of chlorophyll: the first, which exists in fresh leaves, dissolves in acetic acid with a rich grass-green colour; the second, formed from the first by drying, gives an indigo-blue solution with the same acid; and the solution of the third, which exists principally in the pyrus aria and other dark-leaved plants, is brownish-green. So excessive is the colouring power of this body, that Berzelius has calculated that the entire mass of leaves of a large tree seldom contains ten grains of chlorophyll.

It is known that in autumn the leaves of many trees, as the sorbus aucuparia, cornus sanguinea, &c., assume a fine red colour, while the foliage of others, particularly of forest-trees, becomes bright yellow. Berzelius, who has examined the nature of this change, found the chlorophyll to be replaced in such leaves by a red and a yellow colouring matter, to which he gave respectively the names *Erythrophyll* and *Xanthophyll.* The former is an extractive matter, easily soluble in alcohol and water; by the air it is gradually changed into a brown insoluble matter; with alkalies it forms rich green solutions, and with metallic oxides, green lakes; by acids the red colour is restored; a green leaf containing chlorophyll is, however, not reddened by an acid. It is remarkable, that all trees in whose leaves erythrophyll forms in autumn bear red fruit, as the cherry, currant, &c.

Xanthophyll is a deep yellow, fatty substance, which melts between 100° and 120°; it is insoluble in water, but dissolves copiously in alcohol and ether; its solution, exposed to the air and light, is rapidly bleached: alkalies dissolve it sparingly with a yellow colour, which is bleached by light.

We possess but very little accurate knowledge of the colouring matters of flowers: they constitute a very remarkable group of bodies, closely related to each other, and distinct from the colouring matters that have been as yet examined. It has been stated that the colours of all flowers result from two; one blue (*Anthocyan*), which is soluble in water and alcohol, reddened by acids, rendered green by alkalies, and from these changes producing the red, and all intermediate shades of purple and violet; the yellow substance (*Anthoxanthine*) is likewise easily soluble in alcohol and water, and is coloured intensely blue by oil of vitriol. These substances possess most analogy to hematoxylin and to safflower-yellow; but it is highly probable that a great number of species of colouring matters exist in flowers as they do in woods. The quantity present in the flower is generally so excessively minute, that the accurate examination of their properties is exceedingly difficult

On some general Characters of Colouring Matters, and on the Principles of Dyeing.

In addition to the detailed history of the individual colouring matters, there are a few remarks belonging to them as a class which deserve notice.

Under the heads of indigo and of orceïne, I have described the formation of white compounds, by the action of deoxidizing agents, and that in those, which are the only cases that have been accurately examined, it resulted from the direct combination of hydrogen with the colouring matter. This character of forming a colourless compound with hydrogen appears to belong to all colouring substances. If an infusion of logwood, of cochineal, of violets, of immerin, be rendered acid by muriatic acid, and a slip of zinc immersed therein, the liquor becomes gradually colourless, and on adding ammonia, a white lake is precipitated, consisting of the hydruret of the colouring matter combined with oxide of zinc.

With oxygen all colouring matters appear also to combine to form bodies quite or nearly destitute of colour. Thus, if the chrysorhamnate of silver be boiled in water, metallic silver separates, and oxidized colouring matter dissolves. This illustrates the manner in which colours *fade*, and they are more or less *fugitive*, according as their tendency thus to combine with oxygen is greater. On this principle was founded the old process of bleaching, by exposing the cloth to the conjoined agencies of water, air, and light. The bodies whose colour injured the whiteness of the cloth were gradually changed by oxidation into others, less coloured and more easily removable by washing. In the majority of cases, however, the process is not limited to simple oxidation, but carbonic acid is evolved, and the colouring matter is totally broken up in constitution.

The colour of many substances, as logwood, archil, litmus, indigo, of most flowers, &c., is removed by sulphuretted hydrogen and by sulphurous acid. In these cases there is direct combination, and the colour is restored by expelling the combined gas, by heat, or by a strong acid. For commerce, many bodies, particularly those of a yellow colour, are given a temporary whiteness by stoving or smoking with sulphurous acid, by placing them in a room where sulphur is burned; this is done with corn, with straw for hats, with sponges, &c. The sulphurous acid gradually goes off afterward, and the yellow colour returns.

The destruction of colours by means of chlorine is the most important decomposition to which this class of bodies is subject, as on it the modern processes of bleaching all our woven tissues, paper, &c., is founded. Innumerable niceties in the application of coloured patterns on cloth would be impossible, and the art of the calico printer restrained to very narrow limits, were it not for the power which chlorine gives him of removing the original colour from any chosen space, and replacing it by others of various tints. The theory of this action of chlorine, which had been formerly thought to depend upon a mere oxidation of the colouring matter, water being decomposed, has been shown by my results with orceïne, and confirmed by those of Erdman on indigo, to consist in the formation of new substances containing chlorine. The chlorine in some cases replaces hydrogen; in others it combines directly with the colouring matter; in others, again, water is decomposed, and the product, besides containing chlorine, is also more highly oxidized. The

action of chlorine on colouring matter is therefore subjected to the same laws as when it acts upon other organic substances, the series of bodies derived from indigo by chlorine having much analogy to the series of bodies formed with alcohol or olefiant gas.

In relation to the processes of dyeing, colouring substances are divided into two classes, the *substantive* and *adjective*. The substantive colours are those which, being very sparingly soluble in water, and having a strong affinity for the fibre of the cloth, combine directly with it; such are carthamine and indigo; the adjective colours are incapable of so permanently fixing themselves, and the necessary insolubility and affinity for the cloth is given through the intervention of a base with which the colouring substance may combine. The cloth is *mordanted* with alumina (p. 436), or iron (p. 558), or tin (p. 448), or mixtures of these metallic oxides, and as the *lakes* so formed are of different colours, a great variety of tints may be produced. The field of application of substantive colours, also, is greatly enlarged by the use of mordants; the simple colouring matter could, of course, give but its own tints, while it forms, with the bases, lakes of various colours.

The resources of the dyer are by no means limited even by the vast number of coloured substances described in the present chapter. From the mineral kingdom, some of the richest colours are now procured, as has been already noticed in the special history of the salts of chrome, of iron, of copper, of lead, of manganese, and of antimony. It is remarkable, that hitherto no true green colouring matter has been found capable of application in the processes of dyeing, the only greens which exist in nature being the chlorophyll and the green of the stems of buck-thorn (sap-green), neither of which is capable of being attached to cloth: all greens are, therefore, in practice, formed by the superposition of a blue (indigo or Prussian blue) and a yellow (chromate of lead or chrysothammine).

The details of the processes of dyeing and printing in patterns, although embracing some of the most refined applications of the properties of the colouring matters, do not enter into the plan of an elementary and general work, such as this should be.

CHAPTER XXVII.

OF THE VEGETABLE ALKALIES.

The substances now to be described constitute a very remarkable family of bodies. They exist naturally in the plants from which they are derived, and confer upon them their most active medicinal properties; they act as bases, forming, with few exceptions, well-characterized and neutral salts even with the strongest acids, and they are distinguished from most substances of vegetable origin by containing nitrogen. The presence of this element, indeed, has been considered as standing in immediate connexion with the source of their alkaline power, and has given rise to theories of their intimate

constitution, of which I shall notice the most important at the conclusion of their special histories.

Quinine.—($N.C_{20}.H_{12}O_2$) or Qu. Eq. 163·1 or 2039.

The bark of the various species of cinchona contains three vegetable alkalies, combined with the cinchonic and cinchonatannic acids already described. These are quinine, cinchonine, and aricine; of these, the quinine is by far the most important, and is generally extracted from the *yellow bark*. The coarsely-powdered bark is to be boiled with eight or ten parts of water, to which two parts of muriatic acid have been added. When the liquor will dissolve no more, it is to be allowed to cool, and strained; lime is then to be added in very fine powder until the liquor has a marked alkaline reaction; the precipitate is to be collected on a linen cloth, washed once or twice with water, and then dried; from this, boiling alcohol dissolves out quinine and cinchonine; the solution being mixed with water, the alcohol may be distilled off and saved; the residue is to be then neutralized by dilute sulphuric acid, and a slight excess added to form acid salts. On evaporating this liquor to the proper point, the sulphate of quinine crystallizes, while the sulphate of cinchonine remains in solution.

To obtain pure quinine, solution of sulphate of quinine is to be decomposed by caustic potash, and the white curdy precipitate, being carefully dried, is to be dissolved in the smallest possible quantity of spirit of wine. By then allowing it to evaporate spontaneously in a warm place, the pure quinine crystallizes with an atom of combined water.

When heated cautiously, the quinine abandons its crystal-water, and then fuses; its taste is intensely bitter; it requires 200 parts of boiling water for solution, and is almost insoluble in cold water; it dissolves easily in alcohol and ether.

The salts of quinine are generally crystallizable, and soluble in alcohol and water; those with the oxygen acids contain an atom of water, in which they agrée with the salts of ammonia, of melamine, and of anilene; it combines directly with the hydracids.

The *Muriate of Quinine*, (Qu.+H.Cl.), forms pearly needles. It dissolves easily in water; with corrosive sublimate and with bichloride of platinum it forms double salts, soluble in water, and crystallizable.

The *Basic Sulphate of Quinine* is the most important preparation of this base; its manufacture is conducted on a very large scale, according to the process just now given for preparing quinine, or various analogous methods. When crystallized, it contains water, its formula being ($Qu_2+S.O_3+8$ Aq.). It effloresces when gently heated or in very dry air, giving off six atoms of water and retaining two, which cannot be expelled without partial decomposition; it is but sparingly soluble in water, requiring thirty parts of boiling and 740 parts of cold water; it requires eighty parts of cold alcohol, but much less of hot; its crystals are small pearly plates or needles, which, when heated, phosphoresce strongly and fuse; by a strong heat it is, of course, totally decomposed.

The *Neutral Sulphate of Quinine* crystallizes in rectangular prisms

which have the formula (Qu.$+$S.$O_3$$+$8 Aq.). They effloresce easily, dissolve in ten parts of water at 60°, and undergo aqueous fusion at 212°. It is also very soluble in alcohol; though neutral in constitution, its solution reddens litmus.

The sulphate of quinine of commerce is sometimes adulterated with sulphate of lime and with boracic acid, which are known by remaining when the organic substance is burned away, and also with sugar and with margaric acid. The latter is detected by its insolubility in dilute acids; the former by washing the sample with a little water, and precipitating the quinine that is dissolved by a drop of solution of carbonate of soda, when the taste of the sugar is recognised.

Phosphate of Quinine crystallizes in small but very brilliant needles, which are soluble in water and alcohol.

The *Tannate of Quinine* is formed by adding solution of tannic acid or infusion of galls to any salt of quinine. A white precipitate appears, which is totally insoluble in water, but dissolves in acetic and muriatic acids.

Ferroprussiate of Quinine is formed by boiling together one part of sulphate of quinine and one and a half of yellow prussiate of potash with seven parts of water. The newly-formed salt separates as a greenish-yellow oily substance. When the liquor is cold, it is to be poured off, and the ferroprussiate of quinine dissolved in boiling alcohol, from which it crystallizes in greenish-yellow needles by spontaneous evaporation.

The action of chlorine on quinine and its salts is very characteristic. If sulphate of quinine be dissolved in a large quantity of chlorine water, and some water of ammonia added, a deep green precipitate is formed, and the liquor becomes also intensely green. To the body so formed the name *Dalleiochin* has been given. If the green solution be evaporated with contact of air, it becomes dark-red coloured, sal ammoniac is formed, and two bodies, of which one is soluble in alcohol, and the other not; the former is called *Rusiochin*, and the latter *Melanochin*. Formulæ have been proposed for these bodies, but as no security for their accuracy has been given, I think it better not to bring them forward. These reactions, combined with the action of tannic acid, serve as tests for quinine.

Cinchonine.—N.C_{20}.H_{12}O. or Ci. Eq. 155·1 or 1939.

This alkali exists most abundantly in the gray bark (cinchona micrantha), from which it may be obtained by the same kind of process as the yellow bark is subjected to for the extraction of quinine; but it is usually prepared from the mother liquors which remain after the crystallization of the sulphate of quinine, as just now described; from its alcoholic solution it crystallizes in thin colourless prisms; its taste is peculiar and bitter; it requires 2500 parts of boiling water for solution, but dissolves easily in alcohol and in ether. At 330° it fuses, without losing weight. Its salts resemble very closely those of quinine.

Muriate of Cinchonine, Ci.$+$H.Cl., crystallizes easily in brilliant

interwoven needles; it forms double salts with the metallic chlorides, similar to those of quinine.

Sulphate of Cinchonine.—The *basic* sulphate, $Ci_2 + S.O_3 + 2$ Aq., crystallizes in rhombic prisms; it requires fifty-four parts of cold water for solution. The *neutral* salt, $Ci. + S.O_3 + 8$ Aq., is much more soluble, and crystallizes in large, well-formed rhombic octohedrons. The *Tannate of Cinchonine* is a white insoluble powder.

In contact with chlorine, cinchonine forms a dark red solution, and after some time a brown precipitate appears. If iodine and cinchonine be dissolved together in alcohol, and the liquor evaporated spontaneously, a compound crystallizes in saffron-coloured needles, which is described as *Iodide of Cinchonine*, which it cannot be, as hydriodic acid is formed.

Aricine.—$N.C_{20}.H_{12}O_3$ or Ar. Eq. 171·1 or 2139.

This alkaloid is found in the bark known as China de cusco, or arica bark, with which the genuine cinchona bark is often adulterated; the tree yielding it is not known. It is obtained by precisely the same process as cinchonine and quinine are procured from the pale and yellow barks.

It crystallizes in brilliant white needles; it is totally insoluble in water, but easily dissolves in alcohol and ether. These solutions have an intensely bitter taste; by nitric acid it is coloured green; its salts have been but very little examined, but they appear to correspond very closely in constitution and properties to the salts of quinine and cinchonine.

Morphia.—$N.C_{35}.H_{20}O_6$ or Mr. Eq. 293·8 or 3673.

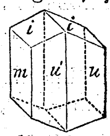
To this body is due, in most part, the medicinal activity of opium, as a substitute for which it is prepared upon a very large scale. The processes adopted in the British pharmacopœias for this purpose are very simple, and deliver a product which, although by no means chemically pure, is yet sufficiently so for all medicinal objects; as they are, however, more especially applied to the preparation of the muriate of morphia, I shall describe them under that head.

To obtain pure morphia, the process invented by Wittstock is perhaps the best. One part of opium, eight of water, and two of muriatic acid are to be digested together for six hours; when the mixture has cooled, the brown solution is to be poured off, and the residue treated twice more with water and acid. The liquors so obtained, being mixed, are to be saturated with common salt, on which they become milky, and after a few hours, a brown clotty precipitate forms; this being removed by the filter, ammonia is to be added in slight excess, and the whole allowed to stand for twenty-four hours. The precipitate which forms in this time is to be collected on a filter, washed with a little water, dried, and digested in spirit of specific gravity 0·820, which dissolves out the morphia. By distillation, the greater part of the spirit is removed, and the morphia, being dissolved in a small quantity of boiling alcohol, crystallizes on cooling. In this process the narcotine is separated by the addition of the common salt, in a solution of which it is insolu-

ble; the meconic acid, codeïne, and thebaïne remain dissolved after the addition of the ammonia in excess, and the other principles present in the opium remain in the mother liquor after the morphia crystallizes.

The process of Merck is founded on the insolubility of morphia in a solution of sal ammoniac, and its solubility in lime-water. Opium is to be digested in three times its weight of water, then expressed, and this repeated three or four times; these solutions being mixed, are brought to boil, and milk of lime added in slight excess; the precipitate which forms is to be collected on a strainer and strongly pressed; the liquor is then to be evaporated until it is about twice the weight of the opium employed, and to be then filtered, brought to boil, and for each pound of opium, one ounce of sal ammoniac added in powder. The morphia separates in crystals, and may be purified by boiling with some lime and ivory black, and precipitation again by sal ammoniac.

Morphia crystallizes in right rhombic prisms, as in the figure, *i*, *u* being primary, and *m* a secondary plane, containing 2 Aq., which they lose by efflorescence in a gentle heat, and become opaque; its taste is strongly and permanently bitter; it is almost insoluble in water, requiring 400 parts when boiling, and separating almost completely as the liquor cools. The solution reacts strongly alkaline; it dissolves readily in alcohol, but very sparingly in ether. It dissolves in solutions of the caustic alkalies or earths. If morphia or any of its salts be brought into contact with nitric acid, they become coloured red; this property belongs also to some other vegetable alkalies, and appears not to be possessed by morphia when absolutely pure. With chlorine water, morphia is first coloured orange-red, and then dissolved. If iodic acid be brought into contact with morphia, it is immediately decomposed, and iodine set free.



If morphia or any of its salts be added to a solution of sesquichloride of iron, the solution assumes a rich blue colour, which is removed by an excess of acid, but returns on the neutralization of it by an alkali. With tannic acid it gives a copious white precipitate. By these remarkable reactions, the recognition of morphia is rendered more simple than that of any other body of its class.

Morphia completely neutralizes the strongest acids, forming salts which are generally soluble and crystallizable.

Muriate of Morphia, $\mathrm{Mr.}+\mathrm{H.Cl.}$, is, for medicinal objects, the most important compound of morphia; its preparation, as directed by the British pharmacopœias, is as follows: the soluble parts of opium having been dissolved out by digestion in water, the united liquors are to be evaporated to the consistence of a sirup, and then cold water added, by which a quantity of feculent matter (apotheme) is separated; the clear liquor is to be decomposed by a slight excess of chloride of lead (London) or of chloride of calcium (Edinburgh). The meconate of morphia, which exists in the opium, being decomposed, meconate of lime or lead is precipitated, and muriate of morphia remains dissolved; the liquor is to be carefully strained and evaporated to a pellicle; on cooling, the salt crystallizes; this is to be pressed between folds of cloth, to remove the

dark mother liquor, and then dissolved in boiling water, digested with ivory black, and recrystallized until the crystals become perfectly white.

The product of this method, although not chemically pure, is sufficiently so for medicinal uses. It contains codeine, and sometimes others of the opium alkaloids. To obtain the pure salt, pure morphia should be dissolved in dilute muriatic acid, and the solution crystallized.

Sulphates of Morphia.—The *neutral* sulphate, which crystallizes in groups of soft needles, and dissolves in twice its weight of water, has the formula $Mr.H.O..S.O_3+5$ Aq. The *Bisulphate of Morphia* does not crystallize.

Acetate of Morphia is formed by dissolving the alkali in acetic acid, or by decomposing muriate of morphia by acetate of lead; it is soluble in water and in alcohol, and, after the muriate, is the most important salt of morphia.

Morphia is precipitated by ammonia and by tannic acid from solutions of any of these salts.

Narcotine.—$N.C_{46}.H_{22}O_{13}$ or Nr. Eq. 5230 or 418.

This alkaloid may be obtained at once from opium by digestion with ether, or when the impure morphia is thrown down by ammonia, ether dissolves out the narcotine from it. It crystallizes in colourless rhombic prisms, which are generally larger than those of morphia; it fuses at 338°, and remains liquid until cooled to 266°, when it congeals as a mass of radiated needles. It is almost insoluble in water, but easily soluble in alcohol and ether; its salts have but little stability, few of them crystallize, and most are decomposed by dilution with much water. By ammonia and tannic acid they are precipitated.

From morphia, narcotine is very easily distinguished by its solubility in ether, insolubility in caustic alkalies and earths, and its not giving the reactions characteristic of morphia with nitric acid or with sesquichloride of iron. But if narcotine be put in contact with sulphuric acid, and oxygen is supplied either by the air or by a trace of nitric acid, it becomes red. Under these circumstances, however, morphia becomes green.

Codeïne.—$N.C_{35}.H_{20}O_5$ or Cdn. Eq. 3573 or 285·8.

This alkali remains dissolved after the morphia, narcotine, and other substances have been precipitated by ammonia. The filtered liquor is to be evaporated to dryness, and digested in solution of potash; a substance remains undissolved, which gradually becomes crystalline. This is to be washed with water, and then dissolved in boiling ether, from which, by spontaneous evaporation, the codeïne separates in colourless prismatic crystals, which contain 2 Aq.

Crystallized codeïne fuses at 300°, giving off its crystal water. It dissolves copiously in water; the solution reacts strongly alkaline; it is insoluble in alkaline liquors, but forms with acids perfectly neutral crystallizable salts. These are precipitated copiously by tannic acid, but not by ammonia; it does not produce any of the reactions described as characterizing morphia. As none of its salts

are employed in pharmacy or medicine, they need not be specially noticed.

Thebaïne.—$N.C_{25}.H_{14}O_3$ or Tb. Eq. 2542 or 203·4.

The watery infusion of opium being treated with milk of lime, so that the morphia may rest undissolved, the precipitate is to be washed with water until it becomes white, and then dissolved in a dilute acid. From this solution thebaïne is precipitated by ammonia. The precipitate being dissolved in ether, and the solution evaporated, pure thebaïne crystallizes in colourless short rhombic prisms, which taste sharp and styptic, and have a strong alkaline reaction. At 300° it fuses, and solidifies then only when cooled to 230°. It is scarcely soluble in water, but abundantly so in alcohol and ether.

By acids thebaïne is decomposed, a resinous substance and a salt of ammonia being formed. In its other characters it completely resembles narcotine.

Narceïne.—The watery solution of opium is to be heated first by ammonia, which throws down morphia, narcotine, thebaïne, and some other bodies, and these being removed by filtrations, the meconic acid and codeïne are to be precipitated by an excess of solution of barytes. The excess of barytes being then removed by a current of carbonic acid gas, the filtered liquor is to be evaporated to the consistence of a sirup and set aside; after some time crystals form, which are a mixture of *meconine* (see p. 610) and *narceïne*. These are separated by ether, which dissolves the meconine, and the residual narceïne being dissolved in alcohol and decolorized by animal charcoal, crystallizes, by the cooling of its solution, in delicate needles.

It tastes bitter, fuses at 200°, and forms a crystalline solid on cooling; it dissolves in 230 parts of boiling water; it is very soluble in alcohol, but insoluble in ether; its solution does not react alkaline, and it is decomposed by strong acids; in its constitution, however, it resembles the true vegetable alkalies, its formula being $N.C_{28}.H_{20}O_{12}$.

Pseudomorphine, $N.C_{54}.H_{18}O_{14}$, occurs but very rarely in opium. For its mode of preparation, when present, I shall refer to the larger systematic works; in its reactions it is absolutely identified with morphia, from which it is distinguished, however, by its composition, by crystallizing in plates, and by not forming any well-characterized salts, although it dissolves very readily in dilute acids

Strychnine.—$N_2C_{44}.H_{22}O_4$ or Stc. Eq. 4355 or 348.

This alkaloid exists associated with brucine in several species of strychos (nux vomica, ignatia, colubrina, &c.), also in the substance used by the natives of Borneo for poisoning their arrows, and termed *Upas-tieuta*, or *Woorara;* it is obtained most easily from the Ignatius's beans, which contain but little brucine; but, as these are not often found in commerce, the nux vomica is most generally employed. The seeds are to be boiled for some time in strong alcohol, which dissolves out a quantity of fatty matter; being then dried in a stove, they are easily reduced to powder; this powder is to be

then boiled two or three times in alcohol, and the liquor distilled until the greater part of the alcohol has come over. To the residue, acetate of lead is to be added as long as any precipitate occurs; by this means more fat, colouring matter, and some organic acids are removed. The filtered liquor is to be then evaporated so far, that from sixteen ounces of nux vomica it amounts to six or eight ounces. To this quantity two drachms of magnesia are to be added, and the whole allowed to stand aside for some days; the precipitate which forms is to be collected on linen, pressed, dried, and dissolved in alcohol, from which the strychnine crystallizes on cooling, while the brucine remains in the mother liquor. As the strychnine, however, is not yet pure, it is to be dissolved in dilute nitric acid, and the solution evaporated to a pellicle. On cooling, the nitrate of strychnine crystallizes in brilliant white, soft, feathery prisms, while the nitrate of brucine separates afterward in large, hard, rhombic prisms. From sixteen ounces of nux vomica, forty grains of nitrate of strychnine and fifty grains of nitrate of brucine may be obtained; from the solution of the pure nitrate in water, the strychnine may be precipitated by ammonia, and, being dissolved in spirit of wine, it crystallizes, by spontaneous evaporation, in small white four-sided prisms.

Strychnine has an intensely bitter, somewhat metallic taste; it requires 7000 parts of cold water for solution; and yet, if one part of this be diluted with 100 parts more of water, this liquor tastes strongly bitter; it is insoluble in absolute alcohol and in ether, but dissolves readily in spirit of wine. With acids strychnine unites, forming well-characterized and crystallizable salts; it differs from the other vegetable alkalies in containing two atoms of nitrogen in its equivalent. With chlorine strychnine gives a white precipitate; also with tannin; when completely pure, it is not reddened by nitric acid, but such as it exists in commerce it generally is so, owing to the presence of traces of brucine.

Muriate of Strychnine, Stc.+H.Cl., crystallizes in crowded rhombic needles, which dissolve readily in water. With corrosive sublimate, with bichloride of platinum, and with cyanide of mercury, it gives insoluble double salts.

Hydrocyanate of Strychnine is obtained by dissolving strychnine in prussic acid; it crystallizes in needles, which are decomposed even by a gentle heat. If solution of sulphocyanide of potassium be added to a solution of any salt of strychnine, the liquor, when agitated, deposites the *Sulphocyanate of Strychnine* in fine radiated needles, which are insoluble in water. By this means one part of strychnine may be recognised in 375 of water, and hence Artus has proposed this reaction as the best medico-legal test for strychnine.

Sulphate of Strychnine forms small cubic crystals, which contain 4 Aq., and are soluble in ten parts of water.

The characters of the *Nitrate of Strychnine* have been described in the method of preparing the alkaloid.

Strychnine is, perhaps, after pure prussic acid, the most intense of poisons. It kills by producing tetanus.

Brucine.—$N_2C_{48} . H_{26}O_8$ or Br. Eq. 408 or 5107.

This substance is found associated with strychnine, as already described, and also in the bark of the false angustura, which is now known to be the strychnos nux vomica, though formerly supposed to be the brucia antidysenterica, whence the name of this alkaloid is derived. Its mode of preparation from the nux vomica has been sufficiently described in the preceding article.

From its solution in spirit, brucine crystallizes in colourless rhombs, containing water, which they abandon on melting at 220°. It dissolves in 850 parts of cold and in 500 parts of boiling water; these solutions react alkaline, and taste intensely bitter; it dissolves readily in alcohol, but is insoluble in ether.

With nitric acid, brucine becomes of a rich red colour, which, on the addition of protochloride of tin, changes to a fine violet; this distinguishes it from the red of morphia, which is completely bleached by protochloride of tin and by sulphurous acid.

With chlorine, brucine gives a yellowish-red, and with iodine a chocolate-brown precipitate.

The salts of brucine have a bitter taste, are generally crystallizable, and give with tannin and with ammonia white precipitates.

The Curara, or *Urari* poison, used in the Indian Archipelago for poisoning arrows, contains a vegetable alkaloid, *Curarine*, which forms a yellow uncrystallizable mass, which dissolves easily in water and in alcohol, but is insoluble in ether; it reacts alkaline, and combines with acids; its salts do not crystallize; its solution is precipitated by tannic acid.

The tree from which curara is derived is not accurately known, but is supposed to be a strychnos.

Delphinine.—$N.C_{27} . H_{19}O_2$ or De. Eq. 2659 or 212·4.—This substance is extracted from the seeds of the stavesacre, *delphinium staphisagria*, by digestion in water, to which some sulphuric acid had been added. The acid liquor is to be decomposed by a slight excess of magnesia, and the precipitate being washed and dried, is to be boiled in alcohol, which dissolves the delphinine. To obtain it quite pure, it is to be redissolved in a dilute acid, boiled with animal charcoal, filtered, precipitated with ammonia, and the precipitate dissolved in alcohol, from which the delphinine separates on cooling as a white crystalline powder.

It is soluble in ether and alcohol; almost insoluble in water; its solution has an intolerably sharp taste; it melts at 250°; chlorine turns it green; oil of vitriol colours it red, and then carbonizes it; its salts are very soluble, but crystallize badly; Courbe states that the stavesacre contains also a substance, *Stephysaine*, ($N.C_{32} . H_{23}O_4$?), which is distinguished by its insolubility in ether; it is a yellow resinous mass, insoluble in water, but dissolving in dilute acids without neutralizing them.

Veratrine.—$N.C_{34} . H_{21}O_6$ or Ve. Eq. 3647 or 289.

This alkaloid is found in the roots of the veratrum album, and in the seeds of the veratrum sabadilla; the best process for its extraction is that given by Vasmer.

The sabadilla seeds are to be infused in water, containing an ounce of oil of vitriol for each pound of seeds, as long as anything is dissolved. The filtered liquor is wine-yellow; it is to be accurately neutralized by carbonate of soda, and evaporated to the consistence of an extract. While yet warm, alcohol is to be poured on it, and digested until everything soluble is taken up. From this solution the alcohol is then to be distilled off, the residue digested in dilute sulphuric acid, and from this liquor the veratria precipitated by carbonate of soda. The precipitate must be redissolved in a dilute acid, digested with ivory black, and again precipitated by a carbonated alkali in order to obtain it pure.

Pure veratrine appears as a white uncrystallized resinous powder; it melts at 230°, reacts alkaline, has no smell, but produces violent sneezing; its taste is exceedingly sharp, but without bitterness; it is insoluble in water, but dissolves readily in alcohol and ether; its salts are mostly crystallizable and neutral, but if mixed with much water they are decomposed, acid being set free, and a basic salt precipitated. Veratrine itself is actively poisonous, and is much used in medicine, but none of its salts are important.

Sabadilline.—$N.C_{20}.H_{13}O_5$ or Sa. Eq. 2351 or 188·1.

This body, which accompanies veratrine, is separated from it by boiling the precipitate produced by the carbonate of soda with water. From the liquor the sabadilline gradually separates in radiated crystalline needles, of a pale rose colour, but when purified it becomes white; its taste is intolerably sharp; it is sparingly soluble in water or in ether, but abundantly soluble in alcohol; it reacts strongly alkaline, and forms crystallizable salts with acids.

Jervine.—$N_2C_{60}.H_5O_6$ or Je. Eq. 5952 or 476.

This alkaloid accompanies veratrine in veratrum album; it is prepared by a process similar to that for veratrine, from which it is separated by the facility with which it crystallizes from its alcoholic solution, and by the very sparing solubility of its sulphate. When pure it is white, easily fusible, totally decomposed at 400°, nearly insoluble in water, but copiously soluble in alcohol. Of its salts, the sulphate, nitrate, and muriate are sparingly soluble in water or in mineral acids; the acetate dissolves readily. Muriate of jervine forms, with bichloride of platinum, a very sparingly soluble double salt. Crystallized jervine contains 4 Aq.

Colchicine.—(Formula not established.)

This alkaloid is obtained from the seeds of the meadow saffron (colchicum autumnale) by digestion in a mixture of weak alcohol and sulphuric acid. The excess of acid in the liquor is to be then neutralized by lime, and the alcohol distilled off. The residual liquor is to be decomposed by carbonate of potash in excess, the precipitate washed, dried, dissolved in absolute alcohol, decolorized by animal charcoal, and gently evaporated, a few drops of water being added. The pure colchicine crystallizes in colourless needles. Its taste is intensely bitter, but not biting, like that of veratrine, nor does it produce the violent sneezing; it is pretty soluble in water, and very soluble in alcohol and ether; its solution reacts feebly alkaline, but neutralizes acids perfectly. Tincture of iodine precipitates it of a rich orange colour. Nitric acid colours it dark violet and blue. Though most abundant in the seeds, all parts of the meadow saffron contain colchicine.

Emetine.—(Formula not established.) This substance exists in all those plants whose roots are sent into commerce under the name of *Ipecacuanha*, or *Hippo*. The roots are to be powdered and digested in ether, by which a fatty substance is taken up. They are then to be boiled with alcohol, the decoction mixed with water, and the spirit distilled off. The residual liquor is to be filtered, and then boiled with magnesia; the precipitate is to be dried and digested in

alcohol, which dissolves the emetine. This solution is to be evaporated to dryness, the residue dissolved in a dilute acid, the liquor boiled with ivory black until completely decolorized, then filtered, and the emetine precipitated by an alkali.

When completely pure, emetine is white and nearly tasteless; it is very poisonous; scarcely soluble in water or in ether, it dissolves readily in alcohol; it possesses strong alkaline properties; its salts are completely neutral, but cannot be crystallized; they dry down to gummy masses. Tannic acid and corrosive sublimate produce white precipitates; iodine, bichloride of platinum, brownish-yellow precipitates with the salts of emetine.

Solanine.—$N.C_{48} . H_{73}O_{28}$ or So. Eq. 7519 or 601.

This alkaloid is found in the berries of the solanum nigrum; in the berries, leaves, and stems of the solanum dulcamara (bitter-sweet) and tuberosum (potato).

The powdered stems of bitter-sweet are to be digested with spirit of sp. gr. 0·865, mixed with one third of sulphuric acid. The liquid is to be supersaturated with milk of lime, the spirit distilled off, the residue washed with water, and what remains treated with dilute sulphuric acid. From the solution thus obtained the solanine is to be precipitated by an alkali, washed with water, dissolved in alcohol, decolorized by animal charcoal, and then obtained by evaporation. It forms a white brilliant powder, of a slightly bitter, nauseous taste; it does not brown turmeric, but restores the blue colour of reddened litmus; it melts a little above 212°; it is almost insoluble in water, sparingly soluble in ether, but copiously in alcohol. With acids it forms neutral salts, which do not crystallize, and are strong narcotic poisons.

The injurious properties of unripe potatoes result from the presence of this body. It exists abundantly in the early shoots (under ground) and buds of the tubers.

Chelerythrine.—(Formula not established.)

This substance is extracted from the roots of the chelidonium majus by digestion with dilute sulphuric acid. The liquor so obtained is to be evaporated and mixed with ammonia. The brown precipitate which falls is to be washed, pressed between folds of paper, and digested in alcohol with some sulphuric acid. The alcoholic solution being mixed with water and the spirit distilled off, the residual liquor is precipitated by ammonia, and the precipitate being washed and dried by pressure, is to be digested in ether, and the ethereal solution evaporated to dryness. The mass so obtained is then digested in dilute muriatic acid, which leaves a resinous substance undissolved. The deep red liquor evaporated to dryness and washed with ether, leaves a mixture of muriate of chelerythrine and muriate of cheledoline, the former of which is dissolved by washing with a small quantity of water, while the latter remains undissolved.

From the solution of the muriate, the chelerythrine is precipitated by ammonia as a white curdy powder. From its ethereal solution it remains as a resinous mass, which remains soft for a long time; it is insoluble in water; its solutions in alcohol and ether are pale yellow. With acids it forms salts of a rich crimson colour, which generally crystallize. Tannic acid produces in their solutions a precipitate soluble in alcohol.

Chelidonine.—$N_3C_{40} . H_{20}O_6$ or Ch.

The preparation of this substance has been in great part described in the preceding article. By digesting the sparingly soluble muriate with ammonia, then dissolving in sulphuric acid, and precipitating with muriatic acid, it is freed from all traces of chelerythrine, and finally the pure chelidonine, separated by ammonia, is dissolved in boiling alcohol, from which it crystallizes, on cooling, in brilliant colourless tables. It is insoluble in water, soluble in alcohol and ether; it tastes bitter, and reacts alkaline; its salts are colourless, and those with the mineral acids crystallize; its solutions give with tannic acid a precipitate.

Aconitine.—(Formula not established.)

The fresh-expressed juice of the monkhood (aconitum napellus) is to be boiled and filtered, and the clear liquor mixed with an excess of carbonate of potash. The

mixture is to be agitated with ether as long as anything is taken up, and by evaporating this solution the aconitine remains. From the dry plant or from the seeds, the aconitine may be obtained by processes similar to those described for veratrine and colchicine.

Aconitine partly crystallizes from its ethereal or alcoholic solution in white grains, but for the most part forms a colourless, vitreous-looking mass; it tastes sharp and bitter, and is intensely poisonous; it reacts strongly alkaline, and neutralizes the strongest acids; alkalies precipitate its solution white; chloride of gold and tannic acid also give white precipitates, and iodine throws it down orange.

Atropine.—$N.C_{34} . H_{23}O_6$ or At.

This alkaloid exists in all parts of the atropa belladonna, but most abundantly in the roots. To prepare it, the fresh roots are to be powdered and digested in alcohol, of specific gravity 0·820. The liquor obtained is to be mixed with lime, in the proportion of one part to twenty-four parts of roots, and laid aside for twenty-four hours with frequent agitation; the mixture is to be then filtered, and the deposite treated with dilute sulphuric acid: the filtered solution is distilled, and the spirit being thus removed, the residual liquor is concentrated by evaporation until it equals one twelfth of the roots employed. To this liquor, when cold, is to be added a strong solution of carbonate of potash, until a dirty brown precipitate occurs, which is to be removed by the filter, and then more carbonate of potash added as long as any precipitate is formed. This last, which is impure atropine, is to be washed with water, then dried, and dissolved in strong alcohol, the solution decolorized by boiling with animal charcoal, filtered, and gradually evaporated, whereby the atropine separates in small white silky prisms.

The taste of atropine is sharp, bitter, and metallic. It dilates the pupil permanently and strongly; if impure, it is brown, does not crystallize, and has a horrible smell, but if quite pure it has no smell; it requires 2000 parts of cold water for solution, but dissolves in thirty-four parts of boiling water, from which some crystallizes by cooling, but the greater part is decomposed; it dissolves readily in alcohol and ether.

The alkaline properties of atropine are feeble; most of its salts are decomposed by boiling with water into ammonia and a substance of an excessively disagreeable smell; this decomposition is instantly effected by the caustic fixed alkalies. Most of the salts of atropine crystallize; tannic acid precipitates their solutions white; the chlorides of platinum and gold, yellow; and iodine, orange-yellow.

Belladonine.—(Formula not established.) The dried root of belladonna is to be mixed with a strong solution of caustic potash and rapidly distilled; the distilled liquor is to be decomposed by bichloride of platinum, and the white precipitate which forms being washed and dried, is to be mixed with carbonate of potash and gently heated. Belladonine sublimes and condenses in colourless rectangular prisms, with a penetrating odour like ammonia; it dissolves in water; the solution reacts alkaline; it is not very poisonous; its salts resemble closely the corresponding salts of ammonia.

It appears to me likely that this substance is a product of the decomposition of the atropine by the caustic potash, and does not exist in the plant.

Daturine.—This substance is obtained from the seeds of the thorn apple (datura stramonium), by the same process as has been described for the preparation of aconitine. From its solution in spirit, it crystallizes in very brilliant colourless groups of needles. When perfectly pure it is inodorous, but when impure it smells disgustingly narcotic; its taste is bitter, and like that of tobacco; it dissolves in seventy-two parts of boiling, and in 250 of cold water, in twenty-one of ether, and in three of alcohol; it melts below 212°, and volatilizes unchanged at a stronger heat in white clouds.

A solution of daturine reacts strongly alkaline, and forms crystallizable neutral salts, which, like pure daturine, are very poisonous. Towards reagents it acts like atropine.

Hyoscyamine.—This alkaloid, which is the active principle of the henbane (hyoscyamus niger and albus), is best prepared from the seeds, in the same way as atropine, except that to the spirit in which the seeds are digested some sulphuric acid should be added. It crystallizes in radiated groups of silky needles, but is more usually obtained as a transparent vitreous mass. In its properties it resembles so perfectly atropine and daturine, that they need not be specially detailed. It neutralizes acids perfectly; its salts are intensely poisonous; they are decomposed very easily, even by boiling with water.

Coneïne.—$N.C_{12}.O_{14}H.$ or Cn. Eq. 1359 or 108·7.

This remarkable substance is the active principle of the hemlock (conium maculatum), in all parts of which it exists, but is more easily extracted from the seeds. These are to be bruised, mixed with one fourth of a strong solution of caustic potash and eight parts of water, and distilled as long as the water which comes over has any smell. This is to be neutralized by dilute sulphuric acid, and evaporated to the consistence of a sirup. The residue is treated two or three times with a mixture of one part of ether and two of alcohol, sp. gr. 0·820, wherein the sulphate of coneïne dissolves. From this solution the ether and spirit are distilled off, then some water added, and the liquor evaporated to dryness. The residue is to be mixed with half its weight of strong solution of potash, and rapidly distilled to dryness. The receiver should be carefully cooled. The oily coneïne should be separated from the watery liquor, and this last distilled again with some lime. If the coneïne contain ammonia, it may be got rid of by exposure for a few hours in vacuo, beside a capsule of oil of vitriol.

Pure coneïne is a colourless transparent liquid, of sp. gr. 0·89; its odour is highly penetrating and nauseating, partly like that of the plant; its taste is disgustingly sharp; it is extremely poisonous. 100 parts of cold water dissolve one of coneïne, and the solution becomes turbid when heated. Coneïne itself dissolves one fourth of water, and this liquor becomes milky even by the heat of the hand; it mixes with alcohol, ether, and oils in all proportions; in close vessels it distils unaltered at 370°, but at a much lower temperature if water be present. When completely anhydrous, coneïne has no alkaline properties, but acts very powerfully if water is present; it saturates acids completely, and has the smallest atomic weight of any organic alkali known. Its salts crystallize but imperfectly; they are decomposed by much water; they dissolve readily in water, alcohol, or a mixture of alcohol and ether, but in pure ether they are insoluble. Their watery solution is precipitated by iodine, saffron-yellow; and by tannic acid, white. Coneïne itself is coloured by nitric acid blood-red; by exposure to the air, especially if warm, coneïne is decomposed; it becomes brown, ammonia is evolved, and a bitter, inodorous, resinous substance is produced, which has no poisonous properties.

Nicotine.—(Formula not established.)

This substance is the characteristic ingredient of tobacco (nicotiana tabacum, and many other species). For its preparation, precisely the same process is to be followed as has been described for coneïne, to which it has a very great similarity. When pure, nicotine is a colourless oily liquid, of a pungent tobacco smell, and a sharp, burning taste; it differs from all other organic bases in mixing with water in all proportions; it mixes also with alcohol and ether. When anhydrous, it gives off white fumes at 212°, and distils at 480°; but the greater part of it is decomposed. If water be present, it distils easily at a much lower temperature.

Nicotine possesses a strong alkaline reaction, and neutralizes acids perfectly. Its salts are generally very soluble, some crystallizable, inodorous, but with a strong tobacco taste. With alkalies they evolve the characteristic odour of the plant.

Menispermine.—$N.C_{18}.H_{12}O_2$. This substance is found in the capsules of the cocculus Indicus, associated with picrotoxine (page 609). The alcoholic extract is to be boiled with acidulated water, and when the picrotoxine has crystallized from the filtered liquor, an excess of alkali is to be added. The precipitate is to be dissolved in alcohol, decolorized by animal charcoal, and evaporated to dryness. The residue is to be digested with ether, which dissolves *Menispermine*, and leaves another body, *Paramenispermine*, undissolved.

From the ethereal solution, menispermine crystallizes in white square prisms. It is tasteless, and not poisonous; it forms neutral crystallizable salts. The paramenispermine dissolves in acids, but does not neutralize them.

Cissampeline exists in the roots of the cissampelos pareira (pareira brava), and is prepared by the same kind of process that has been frequently described. From the evaporation of its ethereal solution, it remains as a yellowish, transparent, vitreous mass, which combines with water, forming a white powder like magnesia. It is very easily decomposed; it is a powerful organic base; its salts form gummy masses, but scarcely crystallize.

Glaucine exists in the glaucium luteum (horned poppy). Its preparation is similar to that of aconitine; it crystallizes in pearly scales; it possesses the same range of properties as the other vegetable bases, and forms crystallizable salts. The horned poppy contains another crystalline principle (*Glauco-picrine*), which appears also to act as a base.

A great number of plants are stated to contain organic bases, which, however, have been as yet so imperfectly examined and described as to render their introduction here useless. Of such substances, the most important are: in the croton tiglium, *Crotonine*, which is crystalline, but is not the active principle; in the æthusa cynapium, *Cynapine*, crystalline; and in the digitalis purpurea, *Digitaline*, which appears most to resemble coneïne.

Of the Constitution of the Vegetable Alkaloids.

From the period of the first discovery of this class of bodies, chemists have endeavoured to ascertain on what depended the basic properties by which they are so remarkably characterized. The discovery, by Liebig, that each equivalent of an organic base contained an equivalent of nitrogen, suggested the very plausible idea that they contained ammonia ready formed, and that in their salts the acid was neutralized by the ammonia, and the organic substance remained combined with the salt, as it had been with the ammonia before. This idea, however, cannot be sustained, as we cannot obtain ammonia from any vegetable alkaloid, unless by processes which totally destroy its constitution, and which, indeed, eliminate ammonia from any organic substance containing nitrogen. Moreover, it is now known that Liebig's rule is not universally true; the equivalents of strychnine and of brucine contain each two atoms of nitrogen, and we know of other organic bases, as melanine, amiline, jervine, and urea, in which the quantity of nitrogen in the equivalent goes much beyond one atom. We may hence conclude that there is no reason to suppose that the vegetable alkalies contain ammonia, or owe their basic properties to its presence.

Some remarkably simple relations of composition occur among certain bodies of this class, which would at first appear to throw light upon their constitution. Thus morphine and codeïne differ in composition only by morphia containing an atom of oxygen more; and if we supposed $(N.C_{35}\,.\,H_{20}O_4)$ to be a compound radical R., then codeïne should be protoxide, R.+O., and morphia deutoxide, R.+2O. In like manner, if we take the cinchona alkalies, we find them to differ only in the quantity of oxygen they contain, and making $(N.C_{20}H_{12})$ a compound radical, cinchonine should be R.+O., quinine R.+2O., and aricine, R.+3O. These remarkable facts might lend considerable support to the idea that these alkaloids are oxygen bases, oxides of compound radicals; but a closer examination of their relations does away with all probability of its truth. Thus, if morphia were R.+2O., then by muriatic acid we should have a bichloride formed, R.+2Cl., and water separated; in place of which, the morphia combines directly with one atom of muriatic acid, and so in all other cases; we cannot find in the compounds of these vegetable alkalies any of the laws which govern the formation of salts by metallic oxides. In addition, the salts formed by these alkaloids with the oxygen acids contain an atom of water, which cannot be expelled without decomposition. In this they resemble ammonia, and I think that it is the only analogy which we can establish by the facts at present known; but whether, in these vegetable alkalies, the nitrogen makes part of a compound radical analogous to amidogene, remains to be decided by future investigations.

CHAPTER XXVIII.

OF THE PRODUCTS OF THE DECOMPOSITION OF WOOD AND THE ALLIED BODIES.

SECTION I.

OF THE SLOW DECOMPOSITION OF WOOD. CONSTITUTION OF ULMINE OF TURF AND COAL.

THE gradual decomposition of the woody tissues of plants gives origin to a class of bodies which had been long confounded under the name of *Ulmine*, but which are now recognised to consist of several distinct substances, differing in their origin, and still more essentially in their properties. From the influence which they exercise in agricultural operations, by forming an element of the soil, and their importance as fuel, by constituting the great mass of turf, they deserve a somewhat detailed notice. I have already stated, that by the action of acids upon sugar (p. 532), lignine, starch, and similar bodies (page 528), brown substances are produced, the composition of which was not definitely established. Mulder has, however, recently reinvestigated the history of this class of bodies, and, from his known accuracy, his results may be looked upon as satisfactory.

When sugar is acted upon by a very dilute acid, and the liquor not allowed to boil, two brown substances are formed, of which one is soluble in solution of carbonate of soda, but the other not. For these bodies the names *Sacchulmine* and *Sacchulmic Acid* may be retained. From the alkaline solution the latter may be precipitated by any stronger acid. These bodies are insoluble in water and in alcohol. The formula of the *Sacchulmine* is $C_{40}H_{16}O_{14}$; that of the *Sacchulmic Acid* is $C_{40}H_{14}O_{12}$. They differ, therefore, in the former containing the elements of water, which, however, cannot be expelled without total decomposition.

If the sacchulmic acid be dissolved in water of ammonia and precipitated by an acid, it retains a quantity of the alkali; and if the ammoniacal solution be decomposed by a metallic salt, the precipitate which forms is a double compound of sacchulmic acid, ammonia and the metallic oxide. It was the unsuspected existence of ammonia in these cases which produced the discordance of former results.

If the sugar be acted on by a stronger acid, and the solution kept boiling for a considerable time, the ulmine bodies disappear, and are replaced by two dark brown or black substances, possessing very analogous properties, the *Saccharo-humine* and *Saccharo-humic Acid* This change takes place more readily if the air have free access. Both are insoluble in water and alcohol; they are separated by alkaline liquors, which dissolve the acid body. From this solution it is thrown down by any stronger acid. The composition of saccha-

ro-humine is expressed by the formula $C_{40}H_{15}O_{15}$; that of the saccharo-humic acid by $C_{40}H_{12}O_{12}$. Like the former bodies, these differ, therefore, in the elements of water.

Mulder found that access of air was not necessary for the formation of sacchulmine or its acid, but that without air no saccharo-humine nor its acid could be produced. In this action, even without access of air, formic acid appears, although but in small quantity; at the same time, glucic acid (p. 534), and another body first described by Mulder, *Apoglucic Acid*, are generated.

When wood remains long in contact with air and moisture, it is gradually converted into a mixture of two brown substances, which, from their having been originally found as a product of the decomposition of elm, are specially termed *Ulmine* and *Ulmic Acid.* The latter is insoluble in alcohol and water, soluble in alkaline solutions; in its natural state it contains ammonia, which can only be expelled by boiling with caustic potash, by which the greater part of the ulmic acid is itself decomposed. Its formula, as derived from the analysis of a specimen furnished by a rotten willow, was $C_{40}H_{12}O_{12}$, being isomeric with saccharo-humic acid, but distinguished from it by many minor characters, especially that when treated with acids it retains twice as much ammonia as the artificial product. Mulder considers the natural ulmine to contain more hydrogen; its formula should then be $C_{40}H_{14}O_{12}$, and by the continued action of the air it should change into ulmic acid. The formation of these bodies from the woody fibre results from the absorption of oxygen and the evolution of carbonic acid and water: thus four atoms of lignine, $C_{48}H_{32}O_{32}$, with fourteen of oxygen, produce $8C.O_2$ with $18H.O.$, and an atom of ulmine, $C_{40}H_{14}O_{12}$.

Another kind of decomposition to which wood is subject is the conversion of the ligneous fibre into a white friable substance, which is formed abundantly in the interior of dead trees; its composition is found to be expressed by the formula $C_{33}H_{27}O_{24}$. It is evidently formed by the lignine combining with oxygen from the air and with the elements of water, and then giving off carbonic acid gas, $C_{36}H_{24}O_{24}$ with $3O.$ and $3H.O.$ forming $C_{33}H_{27}O_{24}$ and $3C.O_2$.

The rotting of wood is, however, by no means necessarily induced by the mere presence of air and water; for lignine may be exposed to these agents for centuries without being altered in any sensible degree. Precisely as in the alcoholic and acetous fermentations, it is necessary that an azotized substance should be present, which, being first decomposed, and forming, probably, crenic and apocrenic acids, communicates the action to the lignine; the albuminous juices which exist in the vessels of the wood act thus as a ferment, and the decomposition of the wood may be prevented by precisely the same methods as counteract the tendency to the fermentation of sugar or of alcohol; any deoxidizing substance, as sulphurous acid; any metallic salt, as corrosive sublimate or bluestone, which may combine with the albumen and render it insoluble, will thus protect wood from decomposition, and are at present extensively used as preservatives against what is technically termed the *dry rot.*

It is by a similar decomposition that the roots and other remains

of plants are converted into a substance which, by virtue of its di rect absorption, or by means of the products of its farther change, contributes powerfully to the nutrition of the succeeding race of plants, and thereby constitutes the essential element of every fertile soil; but though, like ulmine, derived from the rotting of vegetable matters, and for the most part of the same composition, the organic substance of the soil is by no means identical with it. It would even appear, from Mulder's results, that the vegetable constituent of the soil varies in composition according to the nature of the crop. For distinction, I shall apply to the ulmic acid of the soil the name of *Geïc Acid*, proposed by Berzelius. To extract it, the soil is washed with boiling water until this passes away quite clear, and then boiled with carbonate of soda; the brown filtered liquor is precipitated by muriatic acid, and the precipitate boiled with alcohol to dissolve out two organic acids, which will be shortly described. In this state the substance is really an ammoniacal salt, its formula being $C_{40}H_{12}O_{12}+N.H_3+4H.O.$, and even by caustic potash it cannot be completely deprived of ammonia. In the geïc acid of a meadow, the same organic element was found to be united with twice as much ammonia; and in one case, where the substance had been obtained from the soil of an orchard, the geïc acid had the formula $C_{40}H_{12}O_{14}$. The geïc acid, $C_{40}H_{12}O_{12}$, though isomeric with the saccharo-humic and ulmic acids, is proved not to be identical by numerous minor characters, which need not be described here.

In that decomposition of vegetable matter which gives origin to turf, water is present in much greater quantity than in any of the former cases, in many instances the plants being totally immersed, and so matted together, from their mode of growth, that the access of air must be very much prevented. Hence we no longer find in turf the comparatively simple decomposition of the wood into an ulmine and an ulmic acid, but, in addition to these bodies, the turf allies itself to the varieties of coal, in containing several kinds of fossil, resinous, and waxy substances, which are produced by secondary and more complicated reactions. Here it is necessary, however, to describe only such constituents of the turf as are analogous to those already noticed, and for distinction I shall term them *Humous* and *Humic Acids.* The former is found principally in the light, pale brown turf, which is not imbedded in water; the latter, on the contrary, in the heavy black turf, to which water has had free access. They are prepared precisely as noticed for the geïc acid, the turf containing in abundance the same organic acids, soluble in alcohol, as does vegetable soil.

The *Humous Acid* resembles perfectly in its properties the sac chulmic acid, with which it is isomeric, its formula being $C_{40}H_{14}O_{12}$, but it has no tendency to retain ammonia when precipitated by an acid from its combination with that alkali. The *Humic Acid.* on the contrary, combines with ammonia so intimately that they cannot be separated by any reagent; and it even absorbs ammonia in the laboratory, from the small quantity of the gas which may be set free in other operations. As extracted from the black turf, its formula is $C_{40}H_{15}O_{15}+N.H_4O$. It is, therefore, when free from ammonia, isomeric with the saccharo-humine, but differs totally in com-

position from the saccharo-humic acid, with which it is so identified in properties.

The azotized acids which have been noticed as existing in vegetable soil and in turf, are termed the *Crenic* and *Apocrenic Acids*; they derive their origin from the rotting of those elements of the plant which contain nitrogen, as albumen, &c., and are formed, also, in the decomposition of animal substances under peculiar circumstances; thus certain soft minerals, as polishing slate and rottenstone, contain so much organic matter as to be used for food in time of distress in the north of Europe, and Berzelius found this to consist of crenic acid, formed from the bodies of the microscopic animals, whose silicious skeletons constitute the mineral portion of the rock.

These acids were first discovered in mineral springs, whence their name (κρηνη), and are most easily obtained pure from the ochery deposites which form on the sides of the spring, and in which they are combined with oxide of iron and silica. They are separated by means of their copper salts, the white crenate of copper being soluble, while the brown apocrenate of copper is insoluble in a liquor containing free acetic acid; from the copper salts they may be set free by sulphuretted hydrogen.

The *Crenic Acid* is a pale yellow gummy mass, of an astringent taste, very soluble in alcohol and water; its formula is $N.C_{14} . H_{16} O_{12}$; by exposure to the air it changes into *Apocrenic Acid;* this is brown, of an astringent taste, reddens litmus, and is much less soluble in alcohol and water than the crenic acid; its formula is $N_6C_{28} . H_{14}O_6$.

The relations of these acids, and of the several species of ulmine to the nutrition of plants, will be hereafter considered.

The circumstances under which coal is formed have been already noticed generally in p. 476 and 563, but it remains to examine specially the mode of decomposition to which the wood is subjected during that change. The coal appears to require for its production that the ligneous fibre should be in presence of water, with little or no access of air, and that in most cases the temperature shall be elevated. Thus, while ulmine is produced when the woody material is on the surface, or, at least, only immersed in water, the formation of any of the varieties of coal requires the conjoined influence of moisture, of great pressure, arising from the superposition of beds of rock or soil, of a high temperature, given by the proximity of volcanic foci, or generated by the decomposition of the wood itself, and, finally, that the access of air shall be much more limited than in the former cases. Then, according to the age of the geological formation, the nature of the superincumbent rock, and the degree to which the temperature is raised, the coaly material varies in composition. The more recent species (*Lignite* or *Fossil Wood*), which peculiarly belong to the tertiary formations, are characterized by the perfect preservation of the organized structure of the wood, and a more or lees deep brown, but not black colour. Their composition may generally be expressed by formulæ which indicate that, without any absorption of oxygen from an external source, the wood has given off carbonic acid and water.

In the coals of the secondary strata (the proper coal formation) great diversity of constitution exists, depending on local circumstances. It would appear that, where the conversion from lignite into true coal is perfect, the proportion of carbon and hydrogen becomes uniformly $C_{32}H_{12}$, these elements being united with small quantities of oxygen, generally amounting to from three to five atoms. The cannel coal of Wigan, the splint coal of Workington, and the caking coal of Newcastle, have been ascertained, by Johnstone, to be so constituted. Here, also, the change arises from the elimination of the elements of water and carbonic acid from the wood, as $C_{36}H_{24}O_{24}$ produces exactly $4C.O_2$ and $12H.O.$, with $C_{32}H_{12}O_4$.

When the mass of decomposing vegetable matter has been subjected to a very high temperature, as by the direct contact of volcanic rocks, it becomes almost completely carbonized, and the variety of coal termed *Anthracite* is formed. The small quantity of hydrogen and oxygen which anthracite contains, can only be referred to traces of the proper coal that have escaped decomposition, and if pure, it would be a *Mineral Coke*, identical in nature with the coke artificially prepared.

The formulæ here given as expressing the constitution of the products of the decomposition of wood, are to be considered only as illustrative of the kind of reaction which goes on between its elements; for none of these products are pure chemical substances; they form no definite compounds; they have no precise equivalent number, and hence it is only for illustration that a formula can be legitimately employed to express their composition.

The following table contains the ordinary composition of the most important varieties of coal and turf. The numbers given were selected from those obtained in the analyses by Richardson and Regnault.

Kind of Fuel.	Carbon.	Hydrogen.	Oxygen and Nitrogen.	Ashes.	Economic Value of 100 Parts.
Turf	58·09	5·93	31·37	4·61	171
Lignite	71·71	4·85	21·67	1·77	208
Splint Coal . . .	82·92	6·49	10·86	0·13	262
Cannel Coal . . .	83 75	5·66	8·04	2·55	260
Cherry Coal . . .	84·84	5·05	8·43	1·68	258
Caking Coal . . .	87·95	5 24	5·41	1·40	271
Anthracite . . .	91·98	3·92	3·16	0 94	273

At the same time that the great masses of fossil fuel are thus generated by the decomposition of wood, a great number of other products make their appearance, which, although much inferior in quantity, possess, at least in some cases, considerable interest. Thus the fire-damp of mines (p. 563) consists in most part of marsh gas, but contains in some cases, also, olefiant gas and free hydrogen.

Interspersed through the masses of coal are found small quantities of a great variety of bodies, principally carbohydrogens, resembling the oils and stearoptens of plants closely in properties and constitution. Thus *Ozocherit*, or *Fossil Wax*, is found in cavities in the rocks lying upon coal; it is brown, of a foliated structure; it fuses at 143°. *Paraffine*, which is an important constituent of the tar produced in the destructive distillation of wood, is also found associated with coal. It is white, crystallizes in brilliant plates; it fuses at 111°, and may be distilled unaltered; it dissolves readily in ether and alcohol; it is not acted upon by any reagent, whence

its name (*parum affinis*). Both these bodies have the same composition as olefiant gas, consisting of C.H. Many waxy fossil substances are isomeric with oil of turpentine, and one, which is interesting as being the matrix in which the native cinnabar of Idria is imbedded (page 402), has the formula $C_{21}H_7$; it is termed *Idrialine*.

Others of these products are liquid, and frequently issue forth from the surface of the ground, constituting springs, which, from their inflammability, have been invested in uncivilized countries with a sacred character. Such liquids are known as *Rock Oil*, or *Petroleum*. Some specimens of it that have been accurately examined are, like paraffine, isomeric with olefiant gas, while others are isomeric with oil of turpentine, and, absorbing oxygen, are gradually converted into a resinous substance *Asphalt*, for which the formula $C_{40}H_{32}O_6$ has been assigned.

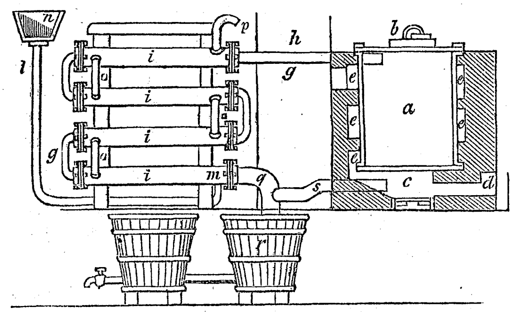
SECTION II.

OF THE PRODUCTS OF THE DESTRUCTIVE DISTILLATION OF WOOD, COAL, AND RESIN.

The results of the action of heat on an organic substance are strictly analogous to those of an imperfect combustion. A quantity of carbon is removed, as carbonic acid, and a quantity of hydrogen, as water. The other products contain, therefore, relatively less oxygen. If the substance upon which we operate be pure, and the heat be carefully managed, the result is in all cases perfectly simple and distinct, as where acetic acid gives acetone and carbonic acid; malic acid gives water, carbonic acid, and maleïc acid; but if the temperature change, another set of reactions occurs, and other products are generated, which arise, properly speaking, from the decomposition of the first. Thus acetic acid gives marsh gas; malic acid gives fumaric acid. Hence, if substances be taken, through which, either from their mass or their non-conducting power, the heat cannot be uniformly diffused, a number of different reactions takes place in different portions at the same time, according to their respective temperatures; the bodies generated in the interior are altered according as they approach the surface, and hence a very high degree of complexity is given to the ultimate results.

When the substances operated on are not pure, but, as common wood, coal, turf, &c., contain various organic bodies of different natures mixed together, it becomes quite impossible to express the precise reactions which occur, and the number of bodies generated becomes very great. It is to the classes of bodies thus produced that I wish to direct attention in the present section, as in all cases where the mode of origin of a pyrogenic product is accurately known, I have described it in connexion with the body from whence it is usually derived.

According as the object of the process is the manufacture of vinegar or of tar, the distillation of wood is very differently managed. For the first, a cast iron cylinder,



a, is built into a furnace, of which *c* is the grate, *d* the fire-door, and *e*, *e*, *e* the flue, which winds spirally round the cylinder, so as to heat it as uniformly as possible. The wood, in pieces which fit accurately the interior of the cylinder, is introduced by an opening in the top, which is then closed by the plate *b*. The volatile and gaseous products of the distillation pass off by the tube *g*, which is bent zigzag, and is surrounded at *i*, *i* by larger tubes, through which a stream of cold water constantly passes. This water is supplied from a reservoir, *n*, by the tube *l*, and,

entering below at *m*, passes from one jacket to another by the cross pipes *o*, *o*, and escapes ultimately above at *p;* this cooling arrangement being a form of Liebig's condensing tube (p. 542), convoluted, as it were, in order to occupy less room. The liquids which are thus condensed collect in the tubs *r*, and the gases which come over are allowed by the cock *t* to issue from the tube *s*, and, being set on fire, play on the bottom of the cylinder, and thus economize a certain quantity of fuel.

The liquid products separate, on standing, into two layers, the upper formed of oily and tarry matters, the lower of water, acetic acid, pyroxylic spirit, &c. By the connecting tube, this heavier liquid passes into the second tub, while the tar remains in the first. The impure acetous liquor is neutralized by carbonate of lime; the acetate of lime decomposed by sulphate of soda or sulphuret of sodium; the acetate of soda crystallized and fused in order to expel the adhering tar, then dissolved, recrystallized, and decomposed by oil of vitriol. Pure acetic acid is thus obtained, which is then diluted with water to the various degrees of strength required in commerce (p. 557).

When the acetous liquor has been neutralized by the lime, it is concentrated by distillation, whereby a spirituous liquid is obtained, which is termed *Pyroxylic Spirit*, and has a close analogy to alcohol in its characters. In this state it is, however, a mixture of a variety of bodies; some of these, as aldehyd and acetone, have been already noticed, and the others will now be described. Mr. Scanlan first recognised the various constituents of the impure pyroxylic spirit, and their history was accurately investigated by Dumas and Peligot, by Löwig and by myself.

The impure pyroxylic spirit having been deprived of water by repeated rectifications over lime, as much chloride of calcium as it can dissolve is to be added to it, and the mixture allowed to stand for a few days. Being then distilled in a water-bath, the body to which the name of pyroxylic spirit is specially applied remains in the retort, combined with the chloride of calcium, while there distils over a mixture of two liquids, *Xylit* and *Mesit*, which are separated from each other by frequent rectification, as their boiling points differ. Besides these three bodies, there exist in the rough liquor an oil, *Methol*, and a solid substance, discovered by Mr. Scanlan, and termed *Eblanine.*

This last body remains behind when the spirit is rectified over lime, from which it is separated by adding muriatic acid, and being then dissolved in boiling alcohol, it crystallizes on cooling; it forms deep orange-yellow needles; it fuses at 350°, and volatilizes in a current of air or of vapour, but is decomposed if heated by itself; it is insoluble in water, but dissolves in alcohol and volatile oils; sulphuric acid colours it indigo blue; its formula is $C_{21}H_9O_4$. No combinations of it are known.

The *Methol* contains no oxygen, its formula being C_4H_3. It boils at 350°, and possesses the general characters of an essential oil.

Xylit resembles alcohol closely in its properties. Its odour is agreeable and ethereal; its specific gravity, 0·816; it boils at 143°; with acids it produces ethereal compounds, which have not been closely examined; its formula appears to be $C_{12}H_{12}O_5$.

Mesit can scarcely be considered as having been as yet obtained pure; in its properties it closely resembles xylit, but has a higher boiling point; its formula has been stated to be $C_6H_6O_2$. I shall have, on another occasion, to notice the probable constitution of these bodies.

The proper *Pyroxylic Spirit* is obtained pure from its combination with chloride of calcium by the addition of water and distillation; by rectification in a water-bath with dry lime it is freed from water. When quite pure, it is a colourless liquid, of a peculiar aromatic smell; it burns with a flame still less luminous than that of spirit of wine; its specific gravity is 0·798; it boils at 140°; its formula is $C_2H_4O_2$; the specific gravity of its vapour is 1·1105; in its action upon other bodies, this substance ranges itself completely with wine-alcohol, and it is hence frequently termed *Methylic Alcohol*, from the Greek words μεθυ and υλη. In the history of its combinations, it will, therefore, be sufficient to fix attention on those points which are more specially characteristic of it, its series being in many respects more complete than that of ordinary alcohol.

Pyroxylic spirit combines with bases and with salts to form compounds similar to the alcoates. It is decomposed by the chlorides of zinc and alcohol, by the fluorides of silicon and boron; methylic ether is evolved, the reactions being precisely as in the case of ordinary alcohol.

When treated with sulphuric acid, the methylic alcohol produces an ether, an organic acid, and a heavy oil, precisely similar to those formed by spirit of wine. But the reaction is much more distinct; all the products remain properly in the series of the methylic alcohol, no gas equivalent to olefiant gas being evolved.

The *Methylic Ether* is, at ordinary temperatures and pressures, a colourless gas, of an ethereal odour; it burns with a blue flame. Water absorbs thirty-seven times its volume of it; its formula is $C_2H_3O.$; it hence is isomeric with wine-alcohol, with the vapour of which it has the same specific gravity, $=1601{\cdot}5$, but its atomic weight is only one half that of alcohol; it combines directly with anhydrous sulphuric acid, forming a heavy oily liquid, and with the other acids to form compound ethers. For the same reasons as have been fully discussed under the head of wine-alcohol, it is assumed to be an oxide of a compound radical, *Methyl*, C_2H_3 or Me., and the formula of the pyroxylic spirit is therefore Me.O.+Aq.

The *Sulphomethylic Acid* is formed precisely as the sulphovinic acid, which it closely resembles in properties, except that it may be obtained crystallized in white needles by cautious evaporation of its solution. Its formula is $Me.O..S.O_3+S.O_3.H.O.$; its salts are generally more permanent, and crystallize more easily than the sulphovinates.

Sulphate of Methyl.—$Me.O.+S.O_3$. This substance passes over as a heavy oil when one part of pyroxylic spirit is distilled with five or six parts of oil of vitriol, and is formed also by the direct union of methylic ether and dry sulphuric acid. It has a strong garlic odour; its specific gravity is 1·324; it boils at 370°. By boiling water or strong bases, it is immediately removed into its constituents. With dry ammonia it forms a white crystalline mass, *Sulphomethylan*, which consists of $Me.O..S.O_3+S.O_2Ad$.

Chloride of Methyl, $C_2H_3Cl.$ or Me.Cl., is formed by heating a mixture of common salt, pyroxylic spirit, and oil of vitriol. A permanent gas is evolved, which may be collected over water, which absorbs but twice its volume of it; it burns with a greenish-white flame.

Iodide of Methyl, $C_2H_3I.$ or Me.I., is prepared by distilling a mixture of phosphorus, iodine, and pyroxylic spirit. On the addition of water to the distilled liquor, the iodide of methyl separates as a heavy oily liquid, of sp. gr. 2·237; it boils at about 112°.

Fluoride of Methyl, $C_2H_3F.$ or Me.F., is formed by heating a mixture of sulphate of methyl and fluoride of potassium, and collecting the gas evolved over water. It is colourless, and burns with a whitish flame, evolving fumes of hydrofluoric acid.

Methylene-mercaptan. Sulphuret of Methyl.—These bodies are prepared precisely as the corresponding substances in the series of ordinary alcohol.

Nitrate of Methyl, $Me.O..N.O_5$, is prepared by distilling nitrate of potash, pyroxylic spirit, and oil of vitriol, mixed together in a capacious retort. The receivers are to be carefully cooled, and a gentle heat applied to the retort to commence the reaction, which then continues to the end without any farther external heat. The product, when purified by redistillation over some oxide of lead, is a colourless liquid, neutral, of an ethereal odour; it burns with a yellow flame; its sp. gr. is 1·182; it boils at 151°. If a drop of it be heated to 300°, it explodes, and this takes place much more easily if there be a quantity; hence its distillation must be very cautiously conducted.

Carbomethylic Acid is formed by passing a stream of dry carbonic acid into a solution of barytes in pyroxylic spirit. Carbomethylate of barytes forms in minute plates, which are insoluble in spirit, but dissolve easily in water. This salt rapidly decomposes into carbonate of barytes, free carbonic acid, and methylic alcohol. With chlorocarbonic acid and sulphuret of carbon, the pyroxylic spirit gives compounds precisely similar to those already described in the series of ordinary alcohol.

Oxalate of Methyl, $Me.O..C_2O_3$, is best formed by distilling a mixture of equal parts of oxalic acid, pyroxylic spirit, and oil of vitriol. The product crystallizes in large rhombic plates; it fuses at 124°, and boils at 312°; it dissolves easily in water and alcohol. With water of ammonia it produces oxamid and methylic alcohol; with dry ammonia it forms a crystalline body, $Me.O..C_2O_3+C_2O_2Ad.$, *Oxamethylan*.

Acetate of Methyl.—$Me.O..Ac.O_3$. Formed by distilling together oil of vitriol, pyroxylic spirit, and acetate of soda. It forms a colourless liquid, which boils at 136°; its specific gravity is 0·919. The substance known as *Mesit* may be considered as a compound of methylic alcohol and aldehyd, $C_2H_3O.+C_4H_3O.$, and the xylit is probably a mixture of that body with the acetate of methyl.

The combinations of methylic ether with the other acids resemble so closely those of vinic ether that they need not be specially described.

Products of the Oxidation of Pyroxylic Spirit.

If pyroxylic spirit be distilled with chromate of potash and sulphuric acid, it is totally converted into carbonic acid and water. If black oxide of manganese be used, and, after the first violent effervescence has ceased, a gentle heat be ap-

plied, a liquid distils over, which, when completely pure, has the formula $C_6H_8O_4$; it boils at 104°; its sp. gr. is 0·855; it is termed *Methylal.*

If pyroxylic spirit be brought into contact with oxygen by means of spongy platinum, as described for ordinary alcohol in p. 554, hydrogen is removed and oxygen absorbed in equivalent proportion, and the methylic alcohol is totally converted into hydrated *Formic Acid*, $C_2H_4O_2$ and 2O. giving 2H.O. and $C_2H_2O_4$. In this reaction there does not appear to be any intermediate state equivalent to that of aldehyd, which body appears to be without a representative in the pyroxylic series, at least, except in combination. For practical purposes, this mode of preparing formic acid is not had recourse to, as it may be derived more easily from the oxidation of most organic bodies.

The formic acid derives its name from existing in a very concentrated form in the common ant (formica rufa), and produces the pain of their sting on being injected into the puncture which the animal makes; it was formerly prepared by distilling the ants with a little water; but the process of Döbereiner is now generally followed. It consists in mixing one part of starch, or sugar, or tartaric acid, with four of black oxide of manganese, four of water, and four of oil of vitriol. Considerable effervescence occurs, owing to the escape of carbonic acid. When this is over, the mixture is to be distilled until four and a half parts have passed over; this acid liquor is to be neutralized by carbonate of soda, and the formiate of soda crystallized by evaporation and cooling. From this salt the formic acid may be obtained in any required degree of concentration, by distillation with oil of vitriol, in precisely the manner described for acetic acid (p. 556).

If sugar, or starch, or barley be simply heated with dilute sulphuric acid until it becomes brown, a certain quantity of formic acid is produced, along with ulmine and ulmic acid. The generation of this acid as a product of the decomposition of prussic acid, of chloral, and of hydrated oxalic acid, has been already noticed.

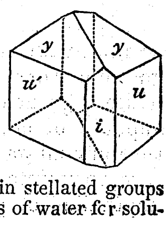
Pure hydrated formic acid is a limpid colourless liquid, which fumes slightly in the air; its odour is intensely pungent; when cooled below 32°, it crystallizes in brilliant plates; it boils at 212°; its specific gravity is 1·235. In this most concentrated form it is an absolute caustic if applied to the skin, producing a sore very difficult to heal; its formula is $C_2H.O_3+H.O.$, and, like acetic acid, it is supposed to contain a radical, *Formyl*, $C_2H.$ or Fo., and its rational formula to be $Fo.O_3+H.O.$ Combining with water, it forms at least one other definite hydrate, the formula of which is $Fo.O_3+2H.O.$

The resemblance of formic acid to acetic acid is very close, but they are at once distinguished by their behaviour to certain reagents. When heated with an excess of oil of vitriol, it is decomposed, with lively effervescence, into water and carbonic oxide ($C_2H.O_3=C_2O_2$ and H.O.). If a solution of formiate be mixed with a cold solution of nitrate of silver, a white crystalline precipitate of formiate of silver falls, which, when heated, is totally decomposed into metallic silver, water, and carbonic acid, $C_2H.O_3+Ag.O.$ giving $2C.O_2$ with H.O. and Ag. If formic acid be digested on red oxide of mercury, carbonic acid is given off, and a sparingly soluble crystalline formiate of the black oxide of mercury is produced: this, when boiled, is totally decomposed, metallic mercury separating, and carbonic acid and water being evolved.

The alkaline formiates are soluble and crystallizable; that of ammonia crystallizes in right rhombic prisms, which melt at 250°, and sublime without alteration. If its vapour be passed through a red-hot porcelain tube, it is totally converted into prussic acid and water, $C_2H.O_3+N.H_4O.$ giving $C_2N.H.$ and 4H.O.

Formiate of Soda crystallizes in rhombic prisms, which have the formula $Na.O.. Fo.O_3+2\,Aq.$ When heated, it undergoes aqueous fusion, and by a higher temperature is decomposed. A solution of this salt, when boiled with the salts of silver, mercury, gold, palladium, or platinum, precipitates the metal, and is hence useful in analysis.

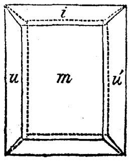
Formiate of Barytes.—$Ba.O..Fo.O_3$. It is obtained in large rhombic prisms, as in the figure, where *u*, *y* are primary, and *i* a secondary plane, which have a bitter taste, and are not altered by the air. It is very soluble in water, but insoluble in alcohol.



Formiate of Lime is easily produced by neutralizing lime with dilute formic acid; it is equally soluble in cold and in hot water, so that it is only obtained crystallized by slow evaporation; it dissolves in ten parts of cold water; it is insoluble in alcohol.

Formiate of Lead.—$Pb.O..Fo.O_3$. If formic acid be added to a solution of acetate of lead, this salt separates after a short time in stellated groups of brilliant needles, which are anhydrous, and require forty parts of water for solu-

tion; it is totally insoluble in alcohol. By the formation of this salt, the formic acid is readily distinguished from the acetic acid, and the two, if present together, may be thus separated.



Formiate of Copper crystallizes in large rhomboidal prisms, as in the figure, where *i*, *u*, *u* are primary, and *m* a secondary plane, which are very regular, transparent, and of a fine, clear blue colour. It effloresces in dry air.

The *Formiates of Mercury.*—That of the red oxide is very soluble; it can only exist at ordinary temperatures; by a very gentle heat it changes into the formiate of the black oxide, and this, when boiled, gives metallic mercury, as already described among the tests for formic acid. The formiate of the black oxide may also be prepared by mixing solutions of formiate of soda and of subnitrate of mercury; it separates in small pearly plates of four and six sides, which may be dried between folds of blotting paper, and have a fine silky lustre.

Chlorides and Iodides of Formyl.—When, under the influence of powerful reagents, the constitution of the compounds of acetyl or elayl is broken up, a series of bodies is generally produced, which are supposed to contain as their radical formyl. Thus, by the action of chlorine on the chloride of elayl, a heavy oily liquid is formed, $C_2H.Cl_2$ or $Fo.Cl_2$, *Bichloride of Formyl;* and by acting on chloral by caustic potash, formic acid is produced, and a heavy oily liquid, which is termed *Chloroform*, and consists of $C_2H.Cl_3$ or $Fo.Cl_3$, being *Perchloride of Formyl.* This, which is the most interesting of these bodies, is easily prepared by distilling alcohol, acetone, or pyroxylic spirit with chloride of lime; it is colourless, of an agreeable ethereal odour; its specific gravity is 1·480; it boils at 141°; the specific gravity of its vapour is 4·116; with an excess of chlorine it gives bichloride of carbon.

Periodide of Formyl. Iodoform, $Fo.I_3$, is produced by adding caustic potash to a solution of iodine in alcohol until it is completely decolorized, but avoiding an excess of alkali; on then evaporating, the iodoform is deposited in brilliant gold-coloured plates; it is insoluble in water, but very soluble in alcohol and ether; it volatilizes at 218°; with potash it gives iodide of potassium and formiate of potash. There exist also bromides, cyanides, and sulphurets of formyl, which do not require notice.

By acting on the methylic ether and on the chloride of methyl with chlorine, Regnault obtained two series of bodies, which follow precisely the same principles of constitution as have been described fully when speaking of wine-alcohol (p. 565). Malaguti also obtained, from the oxalate and acetate of methyl, bodies similar to those generated by chlorine with the ordinary oxalic and acetic ethers, and hence it is only necessary to say that all the conclusions there drawn respecting the nature of these bodies, and the theory of the chlorine radicals, may be applied to explain the origin of the bodies derived from the methylic alcohol also.

Products of the Distillation of Coal.

The products of the distillation of coal in close vessels possess a remarkable analogy to those that have been now described, and, indeed, in many instances, are identical with them. Thus the gaseous products are marsh gas, olefiant gas, and carbonic acid. The liquid products consist of various bodies closely analogous to petroleum, and the solids consist of napthaline and paraffine. The relative proportions of these products vary with the temperature. The lower the heat employed, the less gas, and the more solids and liquids are produced; the higher the temperature, the greater is the quantity of carburetted hydrogen; but, for the purposes to which the practical process is applied, the temperature must not be raised too high, for then the gas evolved would be mostly marsh gas and pure hydrogen, which possess little illuminating power, while a great deal of illuminating power may be derived from the vapours of some highly volatile liquid products. In the manufacture of coal gas for the purpose of illumination, the object is, therefore, to maintain a temperature too high for the production of much napthaline or paraffine, but not high enough to produce hydrogen

or marsh gas, and thus obtain the greatest possible quantity of a gaseous product of olefiant gas and vapours of liquid carbohydrogens.

From the albuminous constituents of the wood, coal always contains a certain, though small quantity of nitrogen, and hence ammonia is evolved in its distillation. The *gas liquor* so obtained is extensively used in the manufacture of sal ammoniac. From the sulphates existing in the plants, or in water which has filtered through the bed of coal, or from iron pyrites, which is generally associated abundantly with the rocks of the coal formation (p. 363), a small quantity of sulphur always exists in coal, which is evolved during the distillation as sulphuretted hydrogen, and requires to be carefully separated from the other gases, which is effected by washing them with the milk of lime, which absorbs also the carbonic acid. The apparatus used for making coal gas does not differ in principle, although very much in arrangement, from that figured in p. 642. The ammoniacal liquor and the tar are collected in the tubs, and the gas, in place of being burned at the orifice of the tube *s*, is conducted to the purifiers, and thence to the gasometers for use.

Most of the substances produced in this process have been already noticed. It only remains now to describe, as briefly as possible, the properties of such others as are important.

Of Napthaline and its Derivatives.—This substance is a very usual product of the decomposition of organic substances by heat; it is obtained abundantly by rectifying coal-gas tar; it crystallizes in white silvery plates; its specific gravity is 1·048; it melts at 136°, and boils at 413°, but sublimes rapidly at much lower temperatures; it burns with a strong smoky flame; its smell is powerful and very peculiar; it is insoluble in water, but abundantly soluble in ether, alcohol, and oils; its formula is $C_{20}H_8$; the specific gravity of its vapour is 4488. It is remarkable for the number of compounds to which it gives rise. When digested with nitric acid, it forms two combinations; the first, *Nitronapthalid*, crystallizes in sulphur-yellow prisms; its formula is $C_{20}H_7 . N.O_4$; the second, *Nitronaphdehyd*, is a white crystalline powder, having the formula $C_{10}H_3 . N.O_4$. Both these bodies are insoluble in water, but dissolve easily in alcohol and ether, from which solutions they crystallize on cooling. When nitronapthalid is distilled with lime, a substance is obtained which resembles eblanine (p. 643) in properties, but consists of $C_{20}H_7O$. Laurent termed it *Oxide of Napthalese.*

Chlorine forms with napthaline a heavy oily liquid, which has the formula $C_{20}H_8 Cl_2$. It gradually evolves muriatic acid gas, and deposites a crystalline substance. This change is effected immediately by heat or by a base. This solid body is termed *Chlornapthelid;* it consists of $C_{20}H_7Cl$. If this be melted and submitted to the continued action of chlorine, hydrogen is removed and a crystalline solid formed, *Chlornapthdehyd*, $C_{10}H_4Cl_2$. By acting on napthaline with an excess of chlorine, and distilling the product, a solid substance is obtained, which crystallizes in large prisms, and has the formula $C_{20}H_6Cl_2$. All of these bodies are insoluble in water, but dissolve in alcohol and ether.

When these chlorine compounds are boiled in nitric acid, a series of substances are obtained containing chlorine and oxygen. Thus from $C_{20}H_8Cl_2$ is formed $C_{20} H_5 . O_3Cl_2$, which is a brilliant yellow crystalline matter, insoluble in water, and melting at 206°. By farther treatment with nitric acid, the *Chloronapthalic Acid* is formed, the formula of which is $C_{20}H_5 . O_6Cl_2$. This body is insoluble in water, but dissolves in ether, and crystallizes, on cooling, in short, brilliant yellow prisms; it melts at 400°, and may be sublimed unchanged. With bases it forms well-characterized salts, which are orange or red-coloured; those of the alkalies and earths are soluble and crystallizable; those of the heavy metals are insoluble in water. In this process there is also formed a substance which does not contain chlorine; it resembles closely benzoic acid; it is termed *Napthalic Acid*, but its composition is not yet decided; another product noticed by Marignac is an acid possessing the remarkable constitution of C.Cl..N.O4.

The action of sulphuric acid on napthaline varies, as the acid is hydrated or anhydrous. In the latter case, sulphurous acid is evolved and a series of products

formed, which have been described by Berzelius as follows: *Sulphonapthaline*, $C_{11}H_8 . S.O_2$, crystallizes in white plates, which melt below 212° to a colourless liquid; *Sulphonapthalid*, $C_{24}H_{10} . S.O_2$, is a snow-white powder, which may be separated from the former by means of its insolubility in cold alcohol. In addition to these bodies there are formed two acids, the *Sulphonapthalic* and the *Sulphonapthic;* they are isolated by taking advantage of the insolubility of the barytes salt of the latter in cold alcohol, and then, by decomposing the barytes salts by dilute sulphuric acid, these organic acids may be obtained crystallized. The *Sulphonapthic Acid* forms soft crystalline scales, of a soapy feel, like talc, which taste bitter and sour. Its formula is $C_{22}H_9 . S_4O_{12}+2$ Aq.; it combines with two atoms of fixed base. The *Sulphonapthalic Acid* forms a hard crystalline mass, which is acid and bitter, inodorous, fusible below 212°; it is very deliquescent; its formula is $C_{20}H_8 . S_2O_5$. The salts of these acids are all soluble in water. There is still another acid product, termed by Berzelius *Sulphoglucic Acid*, the constitution of which is not known.

Notwithstanding that few subjects have been so often investigated as the history of napthaline and its derivatives, there are few bodies whose theory is more obscure. It would appear that all its hydrogen, or at least six atoms of it, is capable of replacement by chlorine or nitrous acid, and there does not exist any distinct character by which the existence of a compound radical, either primitive or derived, as a basis of these combinations, could with reason be assumed. The hypothesis of Marignac is, that napthaline itself is a compound of two carbohydrogens, $C_{16}H_4+C_4H_4$, by the diverse action of reagents upon which the various bodies may be derived; but this idea does not afford sufficient advantages to justify its adoption.

Paranapthaline.—This substance is associated with napthaline in the gas-tar, and is isomeric with it, its formula being $C_{20}H_8$; it differs in its fusing and boiling points, which are very much higher; it may be distilled unaltered; it is insoluble in water, very sparingly soluble in alcohol or ether, but copiously so in oil of turpentine; its relations to other bodies are not well known; with nitric acid it produces a colourless crystalline body, having the formula $C_{15}H_4O_2$.

The liquid products of the distillation of coal have been as yet studied only by Laurent, of the most interesting of whose results, as yet, but the general nature has been published. This liquid, which is properly termed *Gas-naptha*, contains a crystalline solid, which volatilizes without decomposition, and acts as an acid; its formula is $C_{12}H_5O.+$Aq. Its discoverer considers it as a hydrated oxide of a compound radical, which he terms *Phenyl;* it combines with potash and barytes, forming crystalline compounds. With sulphuric acid it forms *Sulphophenic Acid*, $C_{12}H_5O.. S.O_3+S.O_3 . H.O.$, which forms salts resembling the sulphovinates; with chlorine it forms, first, *Chlorophenesic Acid*, $C_{12}H_3 . Cl_2O.+$Aq., which crystallizes in rhombohedrons, and possesses a very nauseous odour; and afterward *Chlorophenic Acid*, the formula of which is $C_{12}H_2 . Cl_3O.+$Aq.

With nitric acid, the hydrated oxide of phenyl produces, first, *Nitrophenesic Acid*, $C_{12}H_3(N_2O_8)O.+$Aq., and by continuing the action, the *Nitrophenic Acid*, $C_{12}H_2(N_3O_{12})O.+$Aq., which is the *Picric Acid* described p. 618, as formed from indigo and salicine. This phenyl series appears, therefore, to be the final result of the oxidation of a great number of organic bodies. As yet, our knowledge of the properties of these bodies is not sufficiently detailed to justify any discussion of their nature, but the connexion with the bodies derived from indigo is exceedingly remarkable. If we consider the radical as $C_{12}H_5$, then amilene is *Amidide of Phenyl*, and all the characters of its salts are easily explained. The substance termed by Laurent *Chloralbine*, $C_{12}H_6Cl_2$, is probably $C_{12}H_5Cl.+H.Cl.$

In preparing olefiant gas for the purposes of illumination, by the destructive distillation of resin, a number of substances, some solid, others liquid, are produced, which have been examined by Pelletier and Walter. Those not already described are as follows: *Retisteren*, a white crystalline solid, which melts at 152° and boils at 617°. In its properties it resembles napthaline; its formula is $C_{32}H_{14}$. *Retinol* is a colourless liquid, tasteless and inodorous; specific gravity =0·9; it boils at 460°; its formula is $C_{32}H_{1?}$, being isomeric with benzin; the specific gravity of its vapour is 7·25. *Retinaptha* is a colourless liquid, of an agreeable odour; its specific gravity is 0·86; it boils at 226°; its formula is $C_{14}H_8$. *Retinyl*, also a liquid, boils at 300°; it consists of $C_{18}H_{12}$, being polymeric with mesitylene.

When the gas obtained by the destructive distillation of oil is strongly compressed, a liquid separates, which was found by Faraday to contain three distinct substances. Of these the most abundant was the benzin described already (page 571), as produced in the decomposition of benzoic acid. Of the others, one is known as *Faraday's Quadricarburet of Hydrogen;* it is also formed abundantly in the distillation of caoutchouc; its specific gravity is 0·627; it boils below 32°; it combines with

chlorine, forming a heavy oil; it is isomeric with olefiant gas, its formula being $C_4 H_4$, and the specific gravity of its vapour is double that of the gas, being 1·962. The third liquid boils at 183°. Its formula is probably C_6H_4, being isomeric with mesitylene and retinyl.

During an elaborate examination of the nature of the tar produced from the destructive distillation of wood, Reichenbach described a number of bodies, of which one, *Kreosote*, has become of much interest, from its remarkable properties, but the others are still very little known. For the preparation of *kreosote*, the tar is rectified by successive distillations, until the oil which passes over becomes heavier than water, and then digested with a solution of caustic potash, which dissolves the kreosote; when this liquor is exposed to the air, it becomes brown, and being then neutralized by an acid, the kreosote separates. This process, of solution in an alkaline liquor and precipitation by an acid, is to be repeated until the solution is no longer browned by exposure to the air; the kreosote is then pure. It is an oily, colourless liquid, with a penetrating odour of smoke; its taste is sharp and burning; its specific gravity is 1·037; it boils at 400°; it burns with a strong smoky flame; with water it unites in two ways: 100 parts of water dissolve 1·25 of kreosote, and 100 parts of kreosote take up ten of water; the solution is quite neutral; kreosote mixes with ether, alcohol, and acetic acid in all proportions. It unites with alkalies and with acids, but without appearing to form any definite compounds, and it is not certain that it has ever been obtained really pure. The formula assigned to it is $C_{14}H_9O_2$.

The most remarkable property of kreosote is, that it coagulates albumen and the colouring matter of the blood, and these bodies are then no longer susceptible of putrefaction. Fibrine, or muscular flesh, immersed in a solution of kreosote for some minutes, has no tendency to putrefy even if exposed to the heat of the sun afterward; from this is its name derived (χρεως σωζω). Kreosote is the antiseptic principle in pyroligneous acid, and in turf or wood smoke. If placed on the tongue, it makes a white mark, with violent pain. Its use as a caustic remedy for toothache is well known.

Kapnomor accompanies kreosote in tar; it is a colourless liquid; it smells like rum; with oil of vitriol it forms a purple solution; it boils at 360°. *Picamar* is also liquid; it boils at 518°; it combines with bases. *Cedriret* crystallizes in fine red needles, insoluble in all liquids except oil of vitriol and kreosote, the former producing a blue, and the latter a purple solution. *Pittakal* forms a dark blue solid mass, which, when rubbed, assumes a golden lustre; it contains nitrogen; it is insoluble in water, but dissolves in acids, and is thrown down again by alkalies. With metallic salts, its solution gives blue precipitates, which may be attached by mordants upon woollen and cotton cloths. The constitution of these bodies has not been examined.

By the action of reagents on the coal-gas naptha, Runge obtained a series of bodies, a re-examination of which would be of the highest interest to science; they are liquid, and appear to possess strong alkaline properties, and generate salts, which with one (*Cyanol*) are of a rich blue colour. They belong apparently to the same class of bodies as anilene.

By the destructive distillation of animal substances, a series of oily bodies is generated, of a strong odour (*Animal Oil of Dippel*, *Oil of Hartshorn*), which is described by Unverdorben as a mixture of several bodies, to which he has given names; but, as we possess no accurate knowledge whatsoever of their properties, I do not think it necessary to give his account of their preparation.

CHAPTER XXIX.

OF THE CHEMICAL PHENOMENA OF VEGETATION.

In the seed of a plant, the germe of the future individual is associated with one or more organs, termed cotyledons, which contain, in general, starch and some form of azotized matter, as albumen, gluten, or legumine, which substances are so disposed in order to supply the nutriment necessary for the development of the embryo, until its organs are fitted for the collection of nutriment from external sources.

The first act of growth in the seed is termed *germination*, and is accompanied by a remarkable change in the constitution of the cotyledonous mass. For perfect germination, it is necessary that the seed be moderately supplied with water and with air, and that it be either in the dark, or exposed but to little light; all these circumstances are perfectly secured by the ordinary mode of sowing seeds in a moistened soil, which shall be so loose as to admit air, and yet exclude the light.

A seed so circumstanced gradually swells to much beyond its original volume, and its temperature rises; it absorbs oxygen from the air, and evolves water and carbonic acid, and the starch of the cotyledon gradually disappears, being changed into sugar. From the point of the seed where the embryo is situated, two shoots spring forth, one of which, the *radical*, takes its direction downward into the soil, while the other, the *plumula*, strikes up towards the air, to become the origin of the stem; according as this growth proceeds, the quantity of sugar in the seed diminishes, and by the time that the radical is fit for the performance of its functions, as root, in absorbing nutriment from the soil, nothing remains of the seed but its ligneous husk, which in some cases completely perishes under ground, but in others rises, and, assuming the functions of leaves (seed-leaves), assists in providing nutriment for the young plants, until the stem has been furnished with leaves by which it may act upon the surrounding air.

This process of germination is artificially produced, for the purposes of the arts, by the operation of *malting;* the grain is steeped in water until it has absorbed the proper quantity of it; it is then spread on the floor of the malthouse, and its temperature prevented from rising too high by the mass being frequently spread out, and new surfaces exposed to the air. When the seed contains the maximum quantity of sugar, that is, when the conversion of the starch is most complete, and yet before much sugar has been assimilated by the germe, which is practically found to be when the radical has grown as long as the grain, but does not project beyond it, the young plant is killed by exposing the malted corn to a current of hot dry air in the malt-kiln, and the malt is then employed as a source of sugar in the fermentative processes of the brewer and distiller.

The saccharine fermentation which thus furnishes nutriment for the young plant in the first stage of its existence, resembles the transformation of starch by means of sulphuric acid, described in p. 528, and is ex-

cited by the presence of a peculiar ferment produced by the decomposition of the vegetable albumen which the seed contains. This active substance is termed *Diastase;* it does not pre-exist in the seed, but is itself produced by the action of the air and water upon the albumen; it is not identical with the ferment which induces the alcoholic fermentation, but they appear to be but successive stages of the decomposition of the same substance. The diastase may be obtained solid by bruising malt with a small quantity of water, and expressing the liquor; to this alcohol is to be added, which precipitates a quantity of unaltered albumen, and on evaporating the filtered liquor to dryness, the diastase remains, though by no means pure; it is a white gummy mass; it is precipitated by infusion of galls and most metallic salts; one part of it rapidly and completely converts a solution of 2000 parts of starch in water, first into dextrine, and finally into grape-sugar. It has been suggested by Saussure that diastase is identical with the substance termed mucin in p. 537, but this is doubtful; it contains nitrogen, and is most probably, as already stated, the first product of the putrefaction of the gluten or albumen.

When the process of germination is over, the plant is found provided, by its roots and leaves, with the means of procuring such nutriment as its future offices require, from the atmosphere and the soil. For the constitution of its proper ligneous tissue, carbon, hydrogen, and oxygen are required, and these serve also for the formation of the majority of its excreted products, as sugar, gum, starch, resin, oils, and acids; but, in addition, nitrogen is required; and although the proportion of nitrogen in any plant is small, compared with that of the other elements, yet it is of great importance as a constituent of the active principles of most medicinal plants, as the vegetable alkalies, amygdaline, &c.; and of still higher interest, as Bousingault has shown the nutritive power of each plant, when used as food, to be proportional to the quantity of nitrogen which it contains. In every plant there exists also certain inorganic elements, acids, and bases, which, though small in quantity, are yet essential to its healthy growth. The examination of the modes, chemical and vital, by which these various substances are supplied to the plant and assimilated by its organs, constitutes an important branch of vegetable physiology, which can here be but superficially sketched; and, in its relation to practice, the manner of supplying these materials so as to favour the growth of plants, and develop their most useful principles, must be the basis of every system of enlightened agriculture.

Of the Assimilation of Carbon by Plants.

In describing the constitution of the atmosphere (p. 269), I have had already occasion to notice the beautiful provision by which the two great classes of organized beings mutually compensate for the change which each produces in its nature, and thus retain it in the condition most conducive to the healthful existence of both. That while the animal, in his respiration, throws off carbonic acid and absorbs oxygen, the plant, from the surfaces of its green leaves, in sunlight, absorbs carbonic acid and gives out oxygen. It only remains here to examine the circumstances of this change with reference to the other functions of the plant.

As water is abundantly absorbed by plants, both with the roots and leaves, the assimilation of carbon from the air should, with it, supply at

once the elements of the woody matter, as well as of those other bodies, as sugar, starch, and gum, which contain oxygen and hydrogen in the proportions to form water. But this respiratory function of the leaves does not in reality possess the simplicity and uniformity of effect which has been just assigned to it. It is found that the absorption of carbonic acid and the liberation of oxygen occur only under the influence of sunlight, and from the green portions of the plant, while the coloured portions, as the flowers and fruits, and even the green leaves during the night, absorb oxygen and give out carbonic acid, thus tending to increase the vitiation of the atmosphere produced by animals in place of counteracting it. The existence of these opposing actions had induced some physiologists to doubt whether they did not neutralize each other, and hence to seek for the source of the carbon of the plant in the action of the roots upon the organic substances of the soil. But the experiments of Daubeny have conclusively established that a healthy plant evolves so much more oxygen in the day than it absorbs during the night, and inversely absorbs so much more carbonic acid during the day than it evolves at night, as may satisfactorily account for the growth of the woody material of the plant, and compensate for the influence of animal respiration and combustion upon the air.

It has been already shown, that the grains of starch, when elaborated by the organs of the plant, possess a structure totally different from that which characterizes bodies constituted in virtue of mere affinity, and more analogous to certain animal organs, as the crystalline lens of the eye. In the different varieties of starch, it is not difficult to trace the gradual transition to lignine, and, as stated in page 530, ordinary wood still retains in the tubes and cells formed by the arrangement of the particles of lignine, a considerable quantity of unaltered starch. In the medulla of various trees, the passage from starch to lignine is still more evident. Now for the formation of starch there are required but water and carbon, its formula being $C_{12}H_{10}O_{10}$, and this I consider as the actual result of the true respiratory process of the plant; carbonic acid being absorbed, and an equal volume of oxygen being exhaled, the carbon is assimilated by the vital power of the plant, and, with the elements of water, produces a substance partially organized in structure, the starch globule. The outer layer of this gradually increasing in density, and water being separated from the internal portion, should give a cell, or, by the reunion of many, a continuous fibre or tube of true lignine. The change being simply the loss of water, the formula of the lignine becomes $C_{12}H_8O_8$. The nature of the starch globule, and, hence, the structure and physical properties of the ligneous fibre, varies in different plants. Thus I consider, in the adult plant, starch to be the first product of the assimilation of carbon and water, that it is already possessed of a low degree of organization, and is, in structure and composition, adapted for the change (growth rather than transformation) into true wood.

By contact with the albuminous or fermentative principles, the starch, whether accumulated in the seed or roots, or distributed throughout the substance of the plant, undergoes changes of an opposite kind. Its organized character is lost; it successively forms gum and sugar. We cannot yet form cane-sugar artificially from starch, but we can have no doubt that it arises, as grape-sugar does, from the catalytic metamorphosis of the starch, arrested, in virtue of the vital power of the plant, at a point

where we cannot seize it in the laboratory. These are the truly nutritious elements of the plant, whether designed for the support of the adult individual, or, collected in proper reservoirs, to serve for the sustenance of the future individual in the seed.

In the conversion of the starch into the numerous secondary products, as acids, colouring matters, oils, &c., the presence of which characterizes the generality of plants, we may find the source of that inverse respiratory action which so much masks the real and simple nutritive process. Of the circumstances of the formation of these bodies, we have an example admirably illustrative of the point, in the conversion of lignine into ulmine. Here, though the change would at first appear to require only the loss of the elements of water, we find it to be much more profound; the constitution of the lignine is totally broken up; oxygen is abundantly absorbed from the air; a quantity of its carbon is carried off as carbonic acid, and a quantity of its hydrogen as water. This action, which may be looked upon as equivalent to the various processes of secretion performed upon the blood by the organs of animals, by which substances adapted to the use or structure of different parts are there deposited, while others unfitted for the purposes of the organized being are thrown off, is carried on by the leaves, probably by all portions of the surface of the plant, and is the source of the continued exhalation of water and carbonic acid which occurs. During the day, and especially in bright sunshine, the assimilating power of the plant being in full action, carbonic acid is taken in, and oxygen given out; during the night, while the plant is in repose, this nutritive action ceases. Through the whole time, however, the process of the secretion is carried on, water and carbonic acid given off, though in such proportion only as to secure at the end of the twenty-four hours an excess of assimilated carbon sufficient fully to secure and account for the rapidity of growth.

The changes of constitution which accompany the ripening of fruit deserve to be considered more in detail than those of which the general nature has been just noticed. If we examine the composition of a young apple, we find it to be nearly tasteless, and to consist of a loose ligneous tissue, in which is imbedded a quantity of ordinary starch; as its growth proceeds, the starch diminishes in proportional amount, and the fruit becomes intensely sour, from the presence of tartaric acid; after some time the acidity becomes of a much less disagreeable kind, and the tartaric acid is found to be replaced by malic acid; and in the next and concluding stage of maturity, this acid disappears, its place being taken by pectine and by sugar. During the whole of these actions, oxygen is absorbed from the air, and water and carbonic acid given off. Their theory is simply indicated: thus starch, which is $C_{12}H_{10}O_{10}$, absorbing 14O., produces 6 Aq. and $4C.O_2$, with tartaric acid, $C_8H_4O_{10}$; and of this, three atoms, absorbing 6O., produce $8C.O_2$ and 4 Aq., with two atoms of malic acid, $2(C_8H_4O_8)$. The change of tartaric to malic acid may also occur without the absorption of oxygen from the air, as $6(C_8H_4O_{10})$ may produce $5(C_8H_4O_8)$ with $8C.O_4$ and 4 Aq.; but as fruits do not ripen in close vessels, unless when they absorb oxygen, the former is more probably the process which actually takes place. The formation of the pectine and sugar from the malic acid may be produced by the absorption of oxygen and the giving off of water and carbonic acid, as $8(C_8H_4O_8)$ with 9H.O. and 5O., produce pectine, $C_{24}H_{17}O_{22}$, sugar, $2(C_{12}H_{12}O_{12})$ with 16C

O_2. That neither pectine nor sugar is derived originally from the starch, is evident, as the starch abounds but in the very earliest stage, and gives place to the tartaric acid, while the increase in quantity of the gelatinous and saccharine matter is proportional to the disappearance of the acid constituents of the fruit.

When our knowledge of the ultimate effect of the complex actions of plants upon the atmosphere was still uncertain, it was considered, and upon very rational grounds, that the plant was indebted for its carbon to the organic substances of the soil, and the necessity for a continued supply of animal or vegetable manure to keep up the fertility of the soil, was thus satisfactorily explained; it was considered that the roots and leaves remaining from the preceding crop, or intentionally mixed up with the soil, were converted, as already described, into ulmine, which, either by itself, or in combination with inorganic bases, was taken up by the absorbing rootlets of the plant, carried into its vessels, and assimilated to the constituents of its tissues; for, in fact, if we examine, at any moment, any kind of fertile soil, we find it to contain abundance of a kind of ulmine (geïc acid, p. 639); we find this ulmine to be a product of the decomposition of the organic substances used as manure; we find that, in barren soils, the ulmine is either absent, or it exists in another isomeric form (humine, &c.), and hence the vegetation appeared distinctly connected with, and attributable to the quantity of geine present. But, notwithstanding such plausible evidence, Liebig has brought forward very strong proof that the action of the ulmine can be but secondary towards the nutrition of the plant. His arguments are derived from the facts: first, that the plant may fully vegetate, though totally unconnected with the ground, as has been proved by experiments upon cellular plants, suspended in the air, and supplied with water; second, that, from the insolubility of every kind of ulmine, either free or when combined with earthy bases, which alone are presented in sufficient quantity in the soil, it cannot be directly absorbed by the rootlets of the plant, which totally reject every kind of solid matter; and, third, that if we compare the quantity of ulmine in a soil before the growth and after the collection of a crop, we find the diminution to be so small when compared with the great quantity of carbon contained in the mass of vegetable matter that has been obtained, as fully to prove the produce of carbon in the crop to bear but an indirect, if any, proportion to the quantity of ulmine in the soil. The true office of the organic matter in the soil appears to be, that, by its gradual decomposition, a constant supply of carbonic acid is afforded to the plant, by which, during the first stages of its development, and while destitute of the expanse of leaf requisite to collect the necessary quantity of nutriment from the air, a more concentrated, and, as it were, richer food is applied to the absorbing roots, and its healthful and rapid growth thus provided for; it is not, therefore, the ulmine of the soil, but the organic matter generally, in changing into ulmine, that may supply carbon to the young plant, the office of the soil-ulmine (geic acid) being different, as will be shortly shown; and, even in this action of the organic matters, the functions of the plant remain the same, being the absorption of carbonic acid and evolution of oxygen.

Assimilation of Nitrogen by Plants.

The organic substances which contain nitrogen belong to two classes;

those of the first, which constitute the active or characteristic principles of many plants, although of much interest in relation to medicine and to abstract science, are of very little importance with reference to the growth of the plant, and its use as food. The bodies whose origin and properties are here of interest, belong to that class of vegeto-animal substances, as albumen, gluten, legumine, of whose extraordinary power in inducing catalytic decompositions of other bodies I have so often spoken; they are found in all parts of the plant, dissolved or diffused through its juices, but especially collected where transformations necessary for growth or germination are to be accomplished. Although present in but small quantity, no function of the plant, in any stage of its existence, could be accomplished without their aid. The conversion of starch into sugar for the nutrition of the germe; of starch or lignine into the vast variety of secretory products in the adult plants; the elaboration of the fruit, its ripening, and even the ultimate destruction of the vegetable tissues, have their origin in a series of actions, induced and maintained by communication from the active fermentation of these azotized materials.

Not merely does the presence of this class of bodies regulate the proper performance of the functions of the plant, but they play an equally important part in favouring the assimilation of vegetable matter when used as food by animals. Bousingault has shown by experiments, to which I shall have occasion again to refer, that in herbivorous animals, the total quantity of nitrogen assimilated for the growth of its muscular and other tissues is derived from, and equal to that contained in the vegetable substances used as food, and that hence, to ascertain the nutritive value of any organic substance, it is only necessary to determine the quantity of nitrogen which it contains. The results so calculated agree with the mean experimental results of the most enlightened agriculturists, within limits as narrow as could be expected in experiments of that kind, and may, by farther research, be brought to still greater accuracy.

Like the carbon, the nitrogen of plants is obtained, in great part, by absorption from the air, but yet it is not merely gaseous nitrogen which is assimilated. The atmosphere always contains a quantity of ammonia, derived from the putrefaction of organic bodies. This is absorbed, and passes into the constitution of a new set of plants, and from them to animals, to be again thrown into the air after their death, and thus circulate from age to age, entering into the constitution of each successive race of organized beings. We cannot refer, however, the total quantity of nitrogen in plants to this one source; for if the produce of one year derived its nitrogen only from the decomposition of the plants of the previous year, the total quantity should be constant; whereas experience teaches us that, by proper methods, the quantity of vegetables produced on a soil may be continuously increased, and for this the nitrogen must be derived strictly by absorption from the air.

Plants vary exceedingly in the facility with which they derive nitrogen from the air, whether by direct absorption of gas or as ammonia. Thus trefoil vegetates and thrives nearly as well when planted in pure sand, and supplied only with water and air, as when sown in ordinary soil; and when fully grown, the quantity of nitrogen is found to be increased twenty-six per cent.; but, on the contrary, wheat grows but slowly under the same circumstances, makes no attempt to flower, and, on analysis, the whole plant is found to contain even a little less nitrogen than

had originally existed in the seed. Wheat has, therefore, no power to assimilate nitrogen from the air, while trefoil possesses that character in probably its greatest vigour. Yet wheat, when fully grown, is rich in nitrogen; its seed is more nutritious than that of any other corn, as it contains more gluten; its nitrogen must, therefore, be derived from another source: it is extracted from the organic matters of the soil.

Without entering here into the question of the nature of manures, which will require especial consideration, it may be stated that, though wheat is thus peculiar in deriving its supply of nitrogen exclusively from the soil, yet all plants do so in a greater or less degree. In the soil, however, the nitrogen is not present uncombined. It is evolved as ammonia from the decomposing organic substances of the manures, and hence animal manures, as producing more of it, are proportionally richer. It has been already noticed (p. 639) that the ulmine of the soil is always combined with ammonia, which it retains with exceeding force. But in presence of strong bases, such as lime, which all fertile soils contain, the ulmine is slowly decomposed, the elements of carbonic acid and of ammonia are eliminated from it, and these both being in a state fit for absorption by the rootlets of the plant, are assimilated, and supply carbon, nitrogen, and water. Independent of the ammonia derived from the organic substances actually contained in the soil, much of that diffused through the atmosphere is carried to the roots of plants by showers of rain, and by the direct absorption of the gas by the porous clay. There are few specimens of clay, especially if they contain iron, which do not give out ammonia when heated, and the absorption occurs with greater power when the clay has been strongly dried. Hence the increased fertility often given to a soil by burning the surface to the depth of a few inches.

Assimilation of Hydrogen.

I have described (p. 653) as the source of the carbonic acid evolved by plants during the night, the conversion of the starchy substance, which I conceive to be that first elaborated by the plant, into the various secretory products, acids, colouring matters, &c. But there are many classes of important vegetable products in which hydrogen so far predominates, that we must conceive for their formation water to be decomposed, and its oxygen to be evolved, either free or in combination with carbon. Of such bodies, glycerine, all of the fixed and many of the volatile oils, wax, and caoutchouc, are examples. The secretory action may thus, in place of opposing that of the respiration of the plant, coincide with it in result, according to the nature of the substances formed, since, if all the carbon of the starch remains in the constitution of the secretion, oxygen is evolved from the water which is decomposed to supply the necessary quantity of hydrogen.

Of the Inorganic Constituents of Plants.

If we make a plant vegetate in water which holds dissolved small quantities of inorganic salts, we find that, as long as the plant remains in health, it exercises upon these salts a remarkable discretionary power of absorption, taking up some and rejecting others, which pass into its substance only when, by the death or weakness of the plant, the liquor enters the tubes by merely physical capillarity. If a plant, whose tissues have

been thus imbibed with saline matters by its own spontaneous power of absorption, be placed in a vessel of pure water, it will be found to give out certain of the saline matters it had taken up, but to retain others. In this manner we may recognise the action of inorganic salts upon plants to be of three kinds: first, directly poisonous, which are rejected by the plant as long as it is in health, and to this class belong most substances poisonous to man; 2d, those to which the plant appears indifferent, which are taken up by it and given off again, without any apparent influence on its growth; and, 3d, those which, when absorbed by the plant, are assimilated to its proper tissues, and are not given up by the plant to water in which it may be immersed.

The bodies of this last class are all combinations of alkalies and earths, and principally with organic acids; they form the ashes of the plant when the organic matter is burned away, and then always possess an alkaline reaction from the formation of carbonates. As a general principle, we may say that each plant requires for its healthy growth inorganic substances in certain quantity and of a certain nature; but replacement of one base by another may occur in certain cases, without positive injury to the plant. Thus the plants which yield soda when grown upon the seashore (salsola, salicornia), if transplanted to the interior, gradually lose the soda, and acquire potash in its place; so that, after a generation, no trace of the former alkali remains. The ashes of oaks or pines grown upon a granitic or basaltic soil contain abundance of magnesia and of potash, while trees of the same species will flourish on a limestone soil, and in their ashes lime will be the predominant ingredient. But these cases of substitution of one base for the other in a plant are still but rare exceptions to the principle, that each kind of plant requires for its vigorous and healthy growth to be supplied with inorganic substances of a specific nature and in certain quantity.

It is this principle which determines the more successful cultivation of certain plants in certain soils. Thus, if we examine the composition of the ashes of wheat, we find abundance of silica, phosphoric acid, magnesia, lime, and potash. If we sow wheat in a soil which contains neither potash nor phosphoric acid, some of the materials necessary for the perfection of the plant being absent, the crop cannot be productive; but if we previously manure the soil with bonedust, with ashes of weeds, or other substances which may supply the necessary inorganic elements, these will be absorbed, and the plants obtain their full development. Even when the quantity of the required inorganic base is but exceedingly minute, it will still be collected by the vital action of the plant in the necessary quantity. Thus, in most sea-plants, iodide of magnesium exists in such proportion as that it affords the universal source of iodine for all technical and scientific objects; and yet that salt, which is excessively soluble, is removed by the plant from the sea-water, which contains but minute traces of it, and is retained in the vegetable tissue by a power which prevents its being washed out again. It is this power of a plant to search for and remove from the soil all traces of those inorganic bases which it most requires, that renders many soils incapable of bearing successive crops of the same kind, without the intermediate application of suitable mineral manures. But if the soil be of such nature as to contain itself those elements, it may become truly inexhaustible for the growth of most species of plant. It is hence that soils formed by the de-

composition of basaltic rocks or of modern lavas are, for every kind of crop, some of the most productive; the facility with which these rocks are decomposed by the action of air and water, provides a constant supply of soil absolutely new, and from the constitution of these rocks, the great variety of their mineral components renders such soil abundant in every element that plants in general require.

Of the Constitution of Soils and of Manures.

From what has been already said, it is easy to judge of the circumstances which render a soil barren or productive, but from the importance of the subject to vegetable physiology and to agriculture, it requires more detailed examination.

The organic elements of the plant being derived for the most part from the atmosphere, the office of the soil, so far as they are concerned, is reduced to supplying to the roots, during those periods when there is not a sufficient expanse of foliage to absorb nutriment from the air, the carbonic acid produced by the gradual rotting of the ligneous matter, and ulmine, and ammonia from the azotized elements of the manure. For this purpose the soil is, in respect to its mineral composition, unimportant; it should be porous, in order to admit of the easy penetration of the rootlets, and to allow free access of oxygen to the organic matter to form carbonic acid; it should yet be close enough to retain moisture in the average intervals of rain, in order that the water necessary for vegetation may not be absent.

These physical conditions are not, however, combined in any one kind of mineral material. If we take a soil of pure sand or of pure limestone, we find them so loose and porous that the water filters off almost immediately after falling, and the plants necessarily perish. If a soil consist of pure clay, its tenacity would be such as totally to prevent the access of air, and all growth of the absorbing filaments of the roots. To combine the two proper conditions of a soil, the clay should be mixed with the porous material, in proportions which vary with the nature of the plant to be cultivated; and thus the simplest soil, in order to fulfil its physical conditions, as supplemental to the atmosphere, should contain two mineral substances, of which one should be clay, and the other lime or silica; and as in practice, unless for some special object, the presence of caustic lime would prove injurious to the absorbing rootlets, this should be present, combined with carbonic acid, as in any of the usual varieties of limestone rocks.

The proper action of the soil, that which it exercises independently of its office in replacing the atmosphere, is to supply to the plant those inorganic constituents, the importance of which have been already shown. For this purpose, a far greater complexity of constitution is required. Thus there is no plant that does not contain both lime and silica, and hence, in the simplest soil, both must be present. There is scarcely a plant whose ashes do not contain a fixed alkali, generally potash; and hence minerals which may yield, by their decomposition, the necessary quantity of that base, should be present in a fertile soil. For most plants, also, magnesia must be supplied; and for many, and especially the various kinds of corn, phosphoric acid. In average soils, most of these bodies are naturally present in the necessary degree. When the soil has originated in the decomposition of granitic or of slaty rocks, the silica, the al

umina, and the potash are abundantly supplied from feldspar and from mica: lime and magnesia also may be derived from associated minerals; but, in general, it is necessary to add lime to such soils, in order that the quantity necessary to full fertility may be present. In purely limestone soils, clay and silicious gravel must be added; and to make up the deficiency in potash, the ashes of other plants and cinders of coal. If the soil be purely silicious, the addition of clay and lime (marl) may bring it to the proper composition.

In these few words are contained the theory of what are termed mineral manures, with few exceptions. In adding lime or marl, bonedust or cinders, to a soil, we either render its physical condition of porosity and tenacity more suitable to the circumstances of the plant, or we supply some ingredient which was either primitively deficient in the soil, or had been removed from it by a previous crop of the same kind. On this last condition is founded also the necessity, in an economic agriculture, of alternating crops which take up from the ground materials of different kinds. Thus, if wheat be grown upon a soil, the rocky substance of which is rich in potash and phosphoric acid, the crops will, after a few years, be unproductive, and the soil impoverished, because the rock decomposes too slowly to supply materials for the wheat as fast as they are required; but if we take from that soil a crop of wheat but once in three years, and interpose some other plant, as trefoil, which takes up but little potash and no phosphoric acid, the soil has time to recover its constitution, and the series of crops, thus arranged in rotatory order, so far from impoverishing the soil, may bring it to a higher degree of richness, by the additions made to its azotized organic components by the roots and rejected leaves of the various crops which are left upon it, and the manure derived from the consumption of its produce by animals.

The advantage of a *rotation of crops* may be thus deduced from the necessity of the soil renewing its mineral constituents, by the gradual decomposition of the subjacent rocky matter (subsoil). But the observations of Macaire and Decandolle indicate another and not less important reason for its use. These physiologists have found, that from the rootlets of a plant the same process of excretion is carried on as by its stem and leaves, and that brown-coloured substances are exuded, which possess much analogy with tannin, and which are poisonous to plants of the same kind when dissolved in the water with which their roots are supplied. On the other hand, the excretory products of one plant may be used without injury, and even advantageously, for the growth of another plant of a different natural family; and in this respect the grasses and the leguminous plants are most remarkable. It is hence, probably, for example, that wheat unfits the soil for the growth of another crop of wheat, not merely by removing the potash and phosphoric acid which is required for the perfection of its parts, but it also gives out a substance poisonous to a plant of the same kind, but which acts beneficially upon the rootlets of a leguminous plant, favouring its growth, while the soil has time to regain from the subsoil the inorganic materials of which it had been deprived.

The utility of manures may now be easily understood; their action is either as bone-earth, marl, lime, cinders, or silicious gravel, to supply to the soil some mineral ingredient in which it had been deficient, or to provide, as by the ordinary vegetable or animal manures, soot, &c., or-

ganic matter, which, by its decomposition, may give out carbonic acid and ammonia for the nutrition of the young plants. In some few cases the action of manures is more indirect; thus the leguminous plants (trefoil) require but little inorganic matter, but much ammonia, and yet there is no manure so efficient in the promotion of their growth as plaster of Paris (sulphate of lime). The plant, however, contains no sulphate of lime; it is not absorbed. The action of this manure appears to be, as was first suggested by Liebig, that, acting on those substances of the ulmine family which always retain a large quantity of ammonia intimately united in the soil, it forms, by double decomposition, ulmate of lime and sulphate of ammonia, which last, being soluble, is easily absorbed by the rootlets of the plant, and the nitrogen assimilated to its tissues.

With regard to organic manures, their great value depends on the proportion of nitrogen they supply. In plants, the great mass of nitrogen is always deposited in organs, as the seed, the tuber, &c., which, for that very reason, are sought after and collected by man, either as food, or for medicinal purposes, from the active (azotized) principles they contain. The roots, stems, and leaves of plants, such as are rejected in the collection of the crop, contain little nitrogen, they being rejected as useless for that very reason. Hence the residue of a former season may manure the land abundantly so far as carbon is concerned, but be quite incapable of supplying nitrogen, and in providing materials for a future abundant crop. The object of the agriculturist must be, so far as organic material is concerned, to supply nitrogen, especially for such plants as the different species of corn, which are incapable of deriving that important element directly from the atmosphere. The value of an organic manure may therefore, for practical purposes, be considered as being measured by the quantity of nitrogen which it contains, and the directness or indirectness of the benefit derivable from it depends upon the manner in which the nitrogen is combined. If mere ammoniacal salts be used, or materials, as animal manures, urine, &c., which soon form ammoniacal salts by their putrefaction, the whole benefit of the manure is given to the crops immediately succeeding its application; but if organic substances be employed which resist decomposition, their nitrogen is evolved but slowly; and though little immediate amelioration be observed from their addition to the soil, their influence is gradually and steadily exerted, and becomes ultimately sensible to the full degree proportional to the nitrogen they contain.

A mode of restoring to the soil the principles it had lost by indiscreet cultivation, is that of *fallowing*. It is a method synonymous with an ignorant and improvident agriculture. The soil having, by over work, lost, on the one hand, some of its essential mineral ingredients, requires time to gather, by the decomposition of the underlying subsoil or rock, a proper quantity of them to supply the elements of the succeeding crops, and having been deprived of its organic elements, especially the nitrogen, it must be allowed to gain from the atmosphere a suitable quantity of ammonia, or by the gradual rotting of the roots of the preceding crop, a quantity of carbonic acid suitable to the wants of that which is to follow. But all of these effects may be more perfectly and more profitably secured by the intervention, in a succession suitably arranged, of other crops, which exercise upon the soil actions alternately opposed. Thus, if we arrange

that wheat, which probably removes from the soil a greater quantity and a greater number of elements than any other crop, shall be succeeded by sown grasses, for forage or hay, which, as they are not allowed to mature their seeds, exercise but little deteriorating action; these, again, by oats, the exhausting power of which is but one sixth that of wheat; then pease or beans manured; that these be followed by barley, the exhausting power of which is one third, and this by a manured green crop, the soil may be brought into a condition superior to that from which we had set out, and the series may be recommenced with wheat, the soil being every season economized. This is but one of the many kinds of rotation which have been found by experienced agriculturists to be as beneficial in practice as theory indicates that they ought to be; and no other reason can be assigned for allowing a field to lie idle every second or third year, but ignorance on the part of the farmer of what could otherwise be done with it.

It remains only to notice, in relation to the theory of the growth of plants, a few additional circumstances connected with the formation of some of their peculiar principles. It is not unusual to hear, from even intelligent agriculturists, objections to the cultivation of certain plants, on the grounds of their exhausting the soil too much. A plant exhausts the soil only in consequence of its forming in proportional quantity some substance, the elements of which are derived from the soil, and which constitute in almost every case the valuable portion of the plant. Wheat exhausts the soil, because it derives therefrom the large quantity of nitrogen which its grain contains; but it is precisely that great quantity of nitrogen which renders wheat more valuable in the market than oats or barley. Tobacco exhausts the soil, because it takes up abundance of nitrogen, with which it forms its nicotine; the more of the active principle the plant produces, the more it exhausts the soil; but in the same proportion, the greater value does it possess when sold. To produce indigo, nitrogen must be supplied to the plants by abundance of rich manure; no crop is more exhausting; but without the nitrogen no colouring matter could be formed, and the plant would be completely worthless. Examples of this kind might be adduced in any number; but these suffice to place in a distinct, though popular aspect, the general principle, that where a plant exhausts the soil. especially as to its nitrogen, it is for the production of the substance which gives the plant its commercial value and importance, and that hence the quantity of manure necessary for the production of an abundant crop is fully repaid by the improved quality of the produce.

Without seeking to enter into the general question of the influence of the physical agents on vegetation, which for its discussion would require more extended limits, and lead to considerations too far removed from chemistry to justify its introduction, I shall, in concluding this sketch of the chemistry of vegetation, notice the peculiar action which light exercises upon plants. It is not merely that it acts as a general stimulus, and thus provokes the activity of nutrition, which determines the ultimate result of the purification of the atmosphere by plants, and that its withdrawal is followed, with plants as with higher beings, by a torpor and tendency to rest, which closes their petals, and folds their leaves at night. But in the production of the coloured parts of plants the agency of light is indispensable. A plant which grows in darkness, as in the gallery of a mine, no matter to what size its form may reach by means of a copious supply

of food, remains soft, its wood unformed, its colour pale; the chlorophyll not being generated, unless under the influence of light. For culinary purposes, precisely this effect is produced by covering up the stems of celery and asparagus, the softness and whiteness admired upon the table being the evidence of the sick and abortive organization of the stem.

The action of light in favouring the production of colour in plants is, however, accompanied by a more material change. The petals, and all coloured parts of plants, except the leaves, absorb oxygen from the air. This is precisely what we find a number of bodies to effect, when passing from their colourless condition to that in which their proper colour is displayed. Thus white indigo becomes blue by absorbing oxygen. Thus rocelline, by absorbing oxygen and giving off water, forms erythrolitmic acid. It is thus, too, by deoxidizing agents, we may remove the colour from logwood, archil, and the flowers of most plants, and restore their tints by again admitting it. Frequently, also, the generation of the coloured substance is accompanied not merely by an absorption of oxygen, but by an escape of carbonic acid; this, which is shown in the laboratory in forming orceïne from erythrine, appears to take place in the tissues of most flowers, which rapidly give out carbonic acid for some time after they have first opened.

In similar actions, carried on in the laboratory by means of chlorine, the influence of light in furthering the removal of hydrogen, and even of carbon, if water be present, is most remarkable, and illustrates the operation of that physical agent in producing the colours of plants in a distinct and satisfactory way. This action has been, however, so fully noticed in describing the general chemical agencies of light (p. 172) and the action of chlorine on colouring matters (p. 622), that I deem it necessary only to refer to what has been there said upon the subject.

CHAPTER XXX.

OF ANIMAL CHEMISTRY

In describing the various classes of organic bodies which have hitherto come under our notice, I have made no distinction as to their animal or vegetable origin, for the point of view under which they were then considered, and the properties which they manifested, were independent of their source. It was thus with ethal, the fatty acids, and colouring matters; and, indeed, in many instances, the same substances were found to be products of both kingdoms of organized nature. In the present chapter I purpose to describe, so far as our accurate knowledge extends, the chemical history of those bodies which I characterized in another place (p. 468) as being rather *organized* than *organic;* as constituting, not merely a product of the vital operations of the being, but the mechanism itself by which these vital operations are carried on; as making part of the tissues essential to its proper organization and life, and as being, while in connexion with the animal, and participating in its life, protect-

ed from the truly chemical reactions of their proper elements, which, after the death of the animal, especially in contact with air and water, rapidly assume simpler forms of union, and, breaking up the complex animal tissue into a crowd of binary compounds, induce the change well known as *putrefaction*.

In connexion with these substances, which form the basis of the tissues and organs of the animal frame, I will bring under survey the processes by which, from the atmosphere, or from the materials of our food, the substance of our organs is continually renewed, their growth provided for, and the conditions necessary for the continuance of health and life maintained. The functions of respiration and of digestion, so far as the chemical phenomena which they embrace are known; the composition of those secretions and excretions, whose agency in the furtherance of those processes has been studied, will here be described; and, finally, the composition of those excretions which have for their office the separation of elements unfit for the nutrition of the beings, or which are not intended for its support.

In each of these divisions I shall add to the description of the composition and properties of these tissues or secretions in the state of health, such facts in reference to the modifications introduced by disease, as have been observed with proper accuracy.

SECTION I.

OF THE COMPOSITION OF THE ANIMAL TISSUES.

A. *Of the Albuminous Materials of the Tissues.*

Of Fibrine.

This substance constitutes the basis of the muscular tissue, and forms an important constituent of the blood. In the latter it exists dissolved during life, but separates after death or extraction from the body, producing, with the colouring material, the phenomenon of coagulation. In the muscles, the fibrine is arranged in a truly organized and living condition, constituting the contractile fibres, in which it is so interwoven with nervous and vascular filaments as to render its isolation impossible. To obtain pure fibrine, therefore, we have recourse to blood, which, if immediately on being drawn it be briskly agitated with a little bundle of twigs, does not coagulate, but the fibrine is deposited on the twigs in soft tenacious masses, which, being washed to remove any adhering colouring matter, and digested in alcohol and ether to remove some traces of fatty substances which adhere to it, constitute pure fibrine, which may be dried by a gentle heat, and appears then as a yellowish opaque mass, hard, tasteless, and inodorous: if it be at all transparent, this results from traces of adhering fat. It is insoluble in water, alcohol, and ether; it absorbs, however, so much water as to treble its weight, and thereby recovers the volume, softness, and flexibility it possessed before being dried. This moisture is not sensible to the hand, but by strong pressure between folds of bibulous paper it may be removed, and the fibrine rendered completely dry. When boiled with water for a great length of time, fibrine is decomposed and dissolves, but it does not form any kind of gelatine.

Fibrine is remarkable for decomposing deutoxide of hydrogen rapidly by catalytic force (p. 235, 258), evolving oxygen. Several of the animal tissues produce this effect, though not containing fibrine. Albumen is, however, totally destitute of it.

Fibrine absorbs cold oil of vitriol, and swells up to a yellow transparent jelly. On the addition of water, it shrinks up and becomes hard; but if all the excess of acid be washed away, the residual mass, which is a neutral compound of fibrine and sulphuric acid, dissolves in pure water. With nitric acid, fibrine evolves nitrogen and nitric oxide, and forms a yellow powder, xanthoproteic acid, to which I shall shortly recur. Tribasic phosphoric acid and acetic acid dissolve fibrine. The solution is precipitated by the mineral acids and by caustic potash, an excess of which last, however, redissolves the precipitate. The mono, or bibasic phosphoric acids, act as sulphuric acid towards fibrine. If perfectly dry fibrine be digested in strong muriatic acid, it swells up, and after a few minutes dissolves into a rich dark blue liquid. No gas is evolved. This blue liquor is precipitated by yellow prussiate of potash.

Fibrine is dissolved even by a dilute solution of caustic potash, and appears thereby to neutralize the alkali almost completely. This solution is coagulated by alcohol and by acids, but not by heat. The precipitates given by acetic and tribasic phosphoric acids are redissolved by an excess.

If sulphate of soda or nitrate of potash be added to newly-drawn blood, its coagulation is prevented; and if fibrine be digested in a strong solution of nitre, it dissolves, forming a thick liquid, which is coagulated by heat, by alcohol, and acids, and is precipitated by the salts of mercury, lead, and copper, and by yellow prussiate of potash. This property of fibrine will again come under notice.

The composition of fibrine is expressed by the formula $C_{800}H_{620} . N_{100} O_{240}+P.S_2$. It contains, besides, minute quantities of lime and magnesia, so that, when incinerated, it leaves 0·77 per cent. of sulphates and phosphates of those bases.

Of Albumen.

This substance is even more extensively distributed through the animal frame than fibrine. Like fibrine, it exists in two conditions, one soluble, and the other insoluble in water; but whereas the fibrine becomes insoluble almost instantly on being withdrawn from the body, albumen may retain that state for an indefinite time, and its history is therefore more complete. In its soluble form it exists in the blood, the egg, in the serous secretions, in the humours of the eye, &c.; in the soluble or *coagulated* form, it constitutes a portion of most of the solid tissues. Albumen derives its name from its constituting the mass of white of egg.

Soluble Albumen.—This is obtained in the solid form by evaporating to dryness, at a temperature which does not exceed 120°, the serum of blood, or white of egg, the membranous investments of the latter having been torn up by triturating with some angular fragments of glass. The dry mass is yellow, transparent, hard, tough, and contains, besides the albumen, the salts and some other constituents of the blood, or white of egg, in minute quantity. These are extracted by digestion in alcohol and ether, which leave the albumen pure. When thus completely dry, it may be heated beyond 212° without passing into the coagulated condition. If digested in cold water, it gradually swells up, and finally dissolves. This solution, when heated to a temperature between 140° and 150°, coagulates. If dilute, the solution may even be heated to 165° without coagulating, and when present in very small quantity, the albu-

men may not separate until the water boils. When once coagulated in this manner, albumen is totally insoluble in water; it is changed into its second form. The solution of albumen is precipitated by alcohol, by acids, and metallic salts, exactly as the solution of fibrine in saltpetre. The only distinction that can be drawn between the two is, that the saline solution of fibrine is partially decomposed by the addition of a large quantity of water.

The precipitates yielded by solution of albumen with metallic salts are mixtures of two distinct substances, one a compound of albumen with the acid, the other a compound of albumen with the metallic oxide; the former is generally somewhat soluble, the latter insoluble; and hence results the application of albumen as an antidote to mineral poisons, as corrosive sublimate and bluestone.

Albumen is also coagulated by many organic bodies, as tannic acid and kreosote, which last acts catalytically, as a very minute quantity of it coagulates a large quantity of albumen, without entering into combination with it.

Coagulated Albumen is obtained by heating serum of the blood, or white of egg, to between 140° and 150°, so that they solidify; washing the mass with water, digesting with alcohol and ether until all soluble is removed, and then drying with care. Thus prepared, it retains some inorganic salts, principally phosphate of lime, from which it may be obtained free as follows: The serum of the blood is to be coagulated by muriatic acid; the coagulum washed with acidulated water, and then so much pure water added as may dissolve it. This solution being then decomposed by carbonate of ammonia, the pure albumen is separated as a flocculent white precipitate.

When dry, it is yellow and transparent; in every chemical character except its relation to deutoxide of hydrogen, it identifies itself with fibrine, and it is hence unnecessary to repeat the details of these reactions; in its composition it is very closely related to it; their organic element is the same, and they differ only in the quantity of sulphur, the formula of albumen being $C_{800}H_{620}.N_{100}O_{240}+P.S_4$. The quantity of ashes remaining from albumen is greater than from fibrine.

The comparative history of these bodies, as now given, leads to considerable doubt as to how far they are chemically distinct, although their physiological characters are so different. Mulder, to whose accurate researches we are indebted for the greater part of our knowledge of the constitution of these bodies, looks upon both as compounds of the real organic substance, which he terms *Proteïne*, with sulphurets of phosphorus. In fact, the sulphur and phosphorus may be removed by very simple methods, and the body (proteïne) which then remains deserves attentive study.

When albumen, fibrine, cheese, or flesh is freed, by digestion in water, alcohol, and ether, from all bodies soluble in these liquids, and, by dilute muriatic acid, all earthy salts have been removed, it is to be dissolved in a dilute solution of caustic potash, and heated to 120°, whereby the sulphur and phosphorus form phosphate of potash and sulphuret of potassium. From the filtered liquor the proteïne may then be precipitated by acetic acid, which must be added only in very slight excess, as otherwise the precipitate would be redissolved.

Proteïne forms grayish-white gelatinous flocks, which, when dried, be-

come hard and yellow, and give an amber-coloured powder. It absorbs water, swells up, and regains the appearance it had before being dried. By long boiling with water it is decomposed and dissolved.

Proteïne dissolves in all very dilute acids, forming neutral compounds which are insoluble in strong acid liquors, and are hence precipitated on the addition of strong acids, except the acetic and tribasic phosphoric acids. With oil of vitriol it combines as described under the head of fibrine, and forms *Proteosulphuric Acid.* It combines also with earthy and metallic oxides, forming insoluble compounds, which are identical in characters with those obtained with albumen.

The composition of proteïne, as found by Mulder, and confirmed by the analyses of its acid and basic combinations, is expressed by the formula $C_{40}H_{32} . N_5O_{12}$. We may evidently consider albumen and fibrine as compounds of proteïne; for if we represent proteïne by the symbol Prt., albumen becomes $Prt_{20}+P.S_4$, and fibrine is $Prt_{20}+P.S_2$. I consider, however, that the state of combination of these bodies requires some farther consideration.

It is found that proteïne constitutes the basis, not merely of the animal substances now under examination, but that it is obtained also from vegetable albumen, gluten, and legumine (p. 538), and constitutes the pure caseous matter of milk, and that the similarity of properties and composition in these bodies is such as to justify us in looking upon them as identical. We have seen that, between albumen and fibrine, the distinctive chemical characters are, if any, so trivial as to leave no firm ground for their distinction in that way; and if we examine the evidence of their being compounds of proteïne with sulphur and phosphorus, we shall find them quite inconclusive. First, it is not certain that such sulphurets of phosphorus exist as $P.S_2$ and $P\ S_4$; second, the compounds of sulphur and phosphorus do not manifest any tendency whatsoever to combination; and, third, in all the reactions of albumen and fibrine, the proteïne on the one hand, the sulphur and phosphorus on the other, act as if they were totally distinct. I look upon albumen and fibrine, while in connexion with the body, as organized and living substances, in whose functions the minute quantity of sulphur and phosphorus may act an important part as a catalytic body. The proteïne I consider, not, with Mulder, as the basis of our tissues, but as the simplest product of their decomposition. It enters in combination with acids and with bases, as indigo or morphia do, which I look upon as totally foreign to the character of a body possessed of vital properties.

Having thus described what I consider to be the true place of proteïne, in relation to albumen and fibrine, I shall briefly notice some of its derived compounds.

Chloroproteïc Acid is formed by passing chlorine into a solution of albumen. It is a white powder. Its formula is $C_{40}H_{31} . N_5O_{12}+Cl.O_4$. By ammonia it is decomposed, nitrogen being evolved, and a white substance formed, *Oxyproteïne*, the formula of which is $C_{40}H_{31} . N_5O_{15}$.

The formation of *Xanthoproteïc Acid*, by the action of nitric acid on fibrine, has been already noticed. It is an orange-yellow powder; when washed from adhering acid, tasteless and inodorous, but reddens moist litmus paper. Insoluble in water, alcohol, and ether, it unites with acids, forming compounds which are pale yellow, and insoluble; with bases it forms soluble salts, generally deep red coloured. Its formula is $C_{34}H_{25} . N_4O_{12}$.

B. *Of the Gelatinous Constituents of the Tissues.*

Of Gelatine.

When the skin, cellular or serous tissues, tendons, and some forms of cartilage, as that of bones, are boiled in water, they dissolve in great part, and form a solution which gelatinizes on cooling. Some of these tissues, as the skin, dissolve easily, and almost completely; others dissolve but partly, and leave behind a quantity of coagulated albumen. In most kinds of cartilage, a very prolonged boiling is necessary to extract any sensible quantity of gelatine. These various tissues are thus found to consist of albumen and gelatine, united in various proportions, and each presenting various degrees of condensation of texture, but by boiling they may be completely separated from each other.

The gelatine is known in commerce as the material of isinglass and of common glue. When pure it is colourless and transparent, very sparingly soluble in cold water, by contact with which, however, it swells up and softens. In hot water it dissolves readily, and on cooling, forms so strong a jelly, that with $\frac{1}{100}$th part it is a consistent solid. It is insoluble in alcohol and ether. When a solution of gelatine is long exposed to the air, or frequently heated and cooled, it undergoes a commencement of putrefaction, and loses its property of gelatinizing. The composition of gelatine, by Mulder's analyses, is expressed by the formula $C_{13}H_{10}N_2O_5$.

The action of reagents on gelatine is in some cases of high interest. By digestion with strong sulphuric acid, as with caustic potash, the same results are obtained. Ammonia is evolved, a white crystalline body (*Leucine*) and a sweet substance (*Sugar of Gelatine*) are formed. They are separated from each other, and from some less important products, by repeated crystallizations. From its alcoholic solution, *Leucine* separates in brilliant colourless plates. It feels greasy, is tasteless and inodorous; heated to 336°, it sublimes totally unchanged. It dissolves in twenty-eight parts of cold water, but requires 625 parts of alcohol, and is insoluble in ether; its formula is $C_{12}H_{12}.N.O_4$. It combines with nitric acid to form *Nitroleucic Acid*, which crystallizes in brilliant needles, and forms with bases neutral salts. Its formula is $C_{12}H_{12}.N.O_4+N.O_5Aq$.

The *Sugar of Gelatine* crystallizes from its solution in alcohol, by spontaneous evaporation, in large prisms, which are colourless, taste sweet, and feel gritty between the teeth. It is decomposed by heat. At 60° it dissolves in five parts of water, but it is sparingly soluble in alcohol and ether. The crystals consist of $C_{16}H_{15}.N_4O_{11}+3$ Aq. It forms, with bases, well-characterized compounds, and unites also with nitric acid.

When acted on by chlorine, gelatine is converted into a white flocculent substance, insoluble in water, but dissolved by an excess of gelatine. Its composition is expressed by the formula $C_{52}H_{40}.N_8O_{29}+Cl.O_4$, consisting, therefore, of four atoms of unaltered gelatine and one atom of chlorous acid. Gelatine is not precipitated either by solutions of ordinary or of basic alum; but if a solution of common salt be also mixed, the gelatine falls down, combined with alumina, as it decomposes the muriate of alumina which is then formed. On this principle is founded the manufacture of white leather, by a kind of tanning with alum.

The most important compound of gelatine is that with tannic acid, which constitutes ordinary leather. This reaction is so distinct, that one

part of gelatine in 5000 of water is at once detected by the infusion of galls. The constitution of the precipitate varies according as one or other of these materials is employed in excess, the tannic acid and gelatine being capable of uniting in at least three different proportions; 100 parts of dry gelatine combine with 136 parts of tannic acid, when the latter is in great excess: this compound contains an atom of each ingredient.

The technical applications of gelatine are numerous, and, for the most part, well known. For glueing together wood, paper, &c., thickening colours, filling up the pores of writing paper, and as isinglass and calves' feet jelly, an article of food, it is abundantly employed; but its most important use is in the manufacture of leather. The skins are cleaned by digestion with lime and scraping with a knife, from the hair and epidermis on the one, and the loose cellular tissue on the other side, and then steeped in pits containing an infusion of oak bark, valonia, sumach, or other of the substances rich in tannic acid (p. 601). At first the tanning liquor is used very weak, as otherwise the surface of the skin would become impervious, and the interior could not afterward be tanned; but having passed through a succession of liquors gradually becoming stronger, the skins are in the last pit interstratified with oak bark, and so, for a considerable time, submitted to the action of the tannic acid in its highest state of concentration, until the conversion into leather is complete throughout the entire substance. They are then removed, and subjected to finishing and cleaning processes, which I need not notice.

Many chemists consider that gelatine is merely a product of the decomposition of albumen or fibrine by boiling water, and not a true constituent of the tissues. I believe this idea to be incorrect on the following grounds: First, pure fibrine, or albumen, gives no gelatine by boiling; second, in the process of tanning, the tannic acid combines with gelatine in a skin which has never been boiled; and, third, that we can easily understand why some tissues give gelatine more easily than others by the different degrees of condensation in their structure; but I rather consider that gelatine bears the same relation to the organized tissue of the skin or cellular membrane that proteïne does to the fibrine of the blood, being really a product of its death and decomposition, though the only representative of it which we can have.

Chondrine.—Those cartilages in which bone is not deposited, are resolved by boiling into a substance possessing much analogy to gelatine, but still distinguished from it by the following properties: it precipitates solutions of alum, sulphate of iron, and acetate of lead, and is precipitated by acetic acid, none of which bodies have any action on ordinary gelatine, which, however, chondrine resembles in all its other characters; in composition, however, it differs, its formula being, by Mulder's analysis, $C_{16}H_{13}.N_2O_7$; it, however, contains a trace of sulphur, its complete formula being $C_{320}H_{260}.N_{40}O_{140}+S$. The physiologist Müller, to whom the discovery of chondrine is due, considers that the skeleton of cartilaginous fishes yields a third variety of gelatine.

C. *Of the fatty Constituents of the Tissues.*

The fatty bodies already described in Chapter XXIII., although contributing essentially to the support of the animal frame, are mere secretions, and do not form any portion of its organized tissues. The sub-

stances properly included under the present head are the constituents of the nervous tissue, such as it is found in the brain, the spinal cord, and nerves.

In the composition of the brain it is possible to distinguish at least three, perhaps five, distinct substances of a fatty nature; the most characteristic and important is termed *Cerebrote:* its mode of preparation can easily be gathered from its characters; it is a white powder, tasteless and inodorous, feeling not at all greasy, but like starch; when heated, it does not melt until it has become brown, and in great part decomposed; it is insoluble in water, sparingly soluble in alcohol or ether when cold, but abundantly when hot; on cooling, it is deposited from its alcoholic solution as a white powder, not at all crystalline; it is not acted upon by alkalies. In composition it resembles albumen, containing a large quantity of nitrogen, with sulphur and phosphorus in minute quantity, but its precise formula cannot be considered as being yet established.

Cerebrol is a liquid reddish oil, having the odour of fresh brain, and a disagreeable rancid taste. It is soluble in all proportions in ether and in oils, but only moderately so in alcohol. It contains the same elements as the cerebrote, and apparently in nearly, if not exactly, the same proportions; but the analyses of Couerbe, who alone has examined their composition, are not authentic enough to be brought forward. The cerebrol is not saponifiable, nor is it in any way altered by digestion with caustic alkalies.

In addition to these two bodies, the brain contains a large quantity of a substance, which, from having been first discovered as a constituent of biliary calculi, is termed *Cholesterine:* it is insoluble in water, but dissolves abundantly in boiling alcohol, from which it crystallizes, on cooling, in brilliant plates; it melts at 290°, and sublimes partially by a stronger heat; it dissolves readily in ether; it is not altered by caustic alkalies; its formula is $C_{36}H_{30}O$. By treatment with hot nitric acid, it is converted into a substance which crystallizes in yellow needles, and forms, with bases, yellow salts. This is *Cholesteric Acid*, the formula of which appears to be $C_{26}H_{20} . N.O_{12}$.

Couerbe has described as constituents of the brain two other fatty bodies, *Cephalot* and *Stearocenot:* they are brown coloured resinous bodies, which, I consider, will most probably, on re-examination of the subject, be found to be impure or decomposed mixtures of cerebrote and cephalol. I hence only indicate their supposed existence. The cholesterine I look upon as being deposited in the brain as ordinary fat is in the cellular tissue, or in the substance of other organs, and not as making up an essential portion of the nervous tissue. This idea is strengthened by the fact that the cholesterine frequently aggregates in the brain in masses, forming one variety of the fatty tumours of that organ.

D. *Of the Saline and Extractive Constituents of the Tissues.*

We find in all the animal tissues small quantities of a great variety of salts, the same as those which will be hereafter noticed as existing in the blood, to the presence of which in the substance of the tissues they are probably due. In the tissue of the bones and teeth, however, these saline matters are deposited in much greater quantity, and in disease and in old age bony deposites occur in all those tissues which yield true gelatine on boiling. The composition of the bones and teeth will be hereafter noticed.

The extractive matters of the tissues, like the extractive matter of plants (p. 612), do not pre-exist as such, but are formed by the decomposition, by protracted boiling in water, of the fibrine, albumen, gelatine, &c., which they really contain. Berzelius has pointed out the existence of a great number of different substances that are thus generated, of which two need here only require notice. For the first, the name *Ozmazome* may be retained, and the name *Zomidine* applied to the second. Ozmazome is soluble in water, and also in absolute alcohol; it cannot be dried by heat, but forms a semifluid of an acid and salty taste, which evolves powerfully the odour of concentrated decomposing urine. Its solution in water is yellow; it is precipitated by the salts of mercury, lead, and tin.

The zomidine is insoluble in alcohol; it dries down to a brown extract, of a strong and agreeable odour of soup. It dissolves in water in all proportions. Its solutions are precipitated by the salts of lead and tin, but not by corrosive sublimate or tincture of galls. When heated it gives out an odour of roasting meat, the taste and smell of which are indeed due to its formation. Both ozmazome and zomidine contain nitrogen.

Of the Composition of the Tissues, and of the Secretions in Health and in Disease.

Having described thus the constituents of the tissues individually, I shall now present such results as have been hitherto obtained as to the quantitative composition of the organized tissues formed by their reunion, their secretory products, and morbid alterations.

Of the Skin, Epidermis, and its Modifications.—The skin of animals is a congeries of finely-constructed organs, sensitive and secretory, imbedded in a peculiar tissue, which is one of those most easily yielding gelatine, whence the process of tanning skins. The relative proportions of solid and liquid matter in a skin freed from adhering fat and cellular membrane, but soft and imbibed with its natural proportions of water, was found by Wienhalt to be,

Proper cutaneous tissues, including blood-vessels and nerves	32·53	100·00.
Albumen	1·54	
Extractive soluble in alcohol	0·83	
Do. soluble only in water	7·60	
Water	57·50	

On the surface of the skin there is secreted a substance, which, though varying in anatomical structure and appearance exceedingly, as it forms the fine epidermis, the nails, proper horn, the tortoise-shell, feathers, hairs, &c., is yet, throughout all their shapes, identical in chemical character, and may be described as the same substance. The best example of horn is that which covers the process of the frontal bone in the ox. It varies in colour, is translucent, tough, and elastic. When heated beyond 212°, it softens without being decomposed, and may then be bent, moulded, and soldered, on which properties many of its uses depend. It is scarcely farther acted on by water even after an ebullition of several days. When treated by strong acids, horn is softened, and becomes soluble in water. Heated with solution of caustic potash, it evolves ammonia, dissolves, and the liquor contains sulphuret of potas-

sium and an organic substance, precipitable by an acid. The composition of these products, or of horn itself, has not been accurately examined.

The principal mass of hair is composed of the same substance as horn, but the colour is due to an oil, which may be extracted by ether. If, by virtue of the sulphur contained in hair, a solution of litharge in lime-water blackens the hair, nitrate of silver blackens the hair also, but by the deposition of the metal. When horn or hair is strongly heated, it fuses, gives off carbonate of ammonia, and gases of a characteristic disagreeable smell; if air be present, it burns with a brilliant flame. The perspiration from the surface of the skin varies in nature according to the part of the body; it is generally acid, contains traces of albumen, fatty matter, and the salts of the blood. It often contains a volatile odorous principle, characteristic of the animal by which it is secreted.

Of the Cellular and Serous Tissues.—These tissues are constituted of gelatinous material, similar to that in the skin, and hence dissolve by boiling in water, being converted into gelatine. In the natural condition of these membranes their surfaces are moistened by a watery liquid, which, accumulating in excessive quantity, gives rise to the dropsies of the cavities or of the cellular tissue. This serum of the cavities is clear and colourless. It reacts alkaline; its specific gravity 1·010 to 1·020; its composition, though liable to fluctuate, is, in general, as found by Berzelius,

Albumen	1·66	1000·00 nearly.
Substance soluble in alcohol	3·32	
Free soda	0·28	
Alkaline chlorides	6·09	
Earthy phosphates	0·09	
Water	987·56	

In the serum of dropsical effusions I have found stearine, elaine, and urea. This observation has also been made by Marchand.

The cells of the cellular tissue, in which fat is usually deposited, are often filled up by an albuminous material, having considerable analogy to caseüm. It is thus that the diffused hardening of the cellular tissue and the local white tumours have their origin. Tendons, aponeuroses, and fibrous membranes are similar in their chemical relations to the cellular and serous tissues.

Of the Muscular Tissue.—From what has been already said of fibrine, it is evidently the essential element of the muscular tissue, and it only remains here to give the numerical results of two analyses of beef muscle, made by Berzelius and Braconnot. They found in 100 parts,

Muscular fibre (with vessels and nerves)	15·80	18·18
Cellular tissue giving gelatine	1·90	
Soluble albumen and colouring matter	2·20	1·70
Alcoholic extract with salts	1·80	1·94
Watery extract with salts	1·05	0·15
Phosphate of lime	0·08	...
Water and loss	77·17	77·03

Composition of the Brain.—The most exact analyses of the brain that we possess are those by Lassaigne. The differently coloured portions differ essentially in their nature, as he found in 100 parts,

	Medullary Substance.	Cortical Substance	
Albumen	9·9	7·5	100·00.
Colourless fat	13·9	1·0	
Red fat	0·9	3·7	
Ozmazome and organic salts	1·0	1·4	
Phosphates	1·3	1·2	
Water	73·0	85·2	

The nerves or spinal marrow have not been specially analyzed.

Composition of the Bones.—Müller has found that, prior to ossification, the cartilage of the bones is in that condition which yields chondrine, although it is afterward totally changed into the gelatine cartilage. In the vertebrated animals with osseous skeletons, the earthy material, in all cases, consists principally of phosphate of lime with some phosphate of magnesia, carbonates of lime and soda, and fluoride of calcium. By digesting a bone in dilute muriatic acid, all of these inorganic salts are removed, and the cartilage remains, preserving perfectly the form of the bone. By burning the bone in a moderate current of air, all animal matter may be consumed, and the earthy material then remains in the form of the bone, and perfectly white; 100 parts of burned bone of the following animals have been found to contain,

	Human Bone.	Beef Bone.	Lion.	Sheep.
Phosphate of lime and fluoride of calcium	86·4	90·70	95·0	80·0
Carbonate of lime	10·3	2·16	2·5	19·3
Carbonate of magnesia	0·3	1·10	2·5	0·7
Carbonate of soda	3·0	5·74		

But these proportions vary in the bones of different individuals of the same kind of animal.

The quantity of animal matter in the bones varies in different classes of animals. In the mammalia it is generally about thirty-three per cent. Thus human and ox bones, deprived of their marrow and periosteum, and dried until they ceased to lose weight, gave Berzelius,

	Human Bone.	Beef Bone.	
Cartilage soluble in water	32·17	33·30	100·00.
Vessels	1·13		
Phosphate of lime and fluoride of calcium	53·04	57·45	
Carbonate of lime	11·30	3·85	
Phosphate of magnesia	1·16	2·85	
Soda and a little common salt	1·20	3·45	

The teeth present, in their constitution, the closest analogy to bone The principal and organized substance of the teeth is indeed true bone, containing, however, less cartilage (twenty-nine per cent.) and more phosphate of lime (sixty-four per cent.) than the other bones. The enamel, which is an inorganic secretion from the upper surface of the bony tooth, is almost destitute of any animal matter, the analyses of Berzelius giving,

	Human Enamel.	Beef Enamel.	
Phosphate of lime and fluoride of calcium	88·5	85·0	100·00.
Carbonate of lime	8·0	7·1	
Phosphate of magnesia	1·5	3·0	
Soda	"	1·4	
Animal matter and water	2·0	3·5	

The proportion of fluoride of calcium is greater in enamel than in common bone, and the animal membrane appears to belong only to the connexion of the enamel with the subjacent bony tissue of the tooth. The

exterior *crusta petrosa* of the teeth, which exists most developed in herbiferous animals, has the same composition as bone.

In the invertebrate animals, the internal skeleton is replaced by an external shell, which contains cartilage, with earthy salts, similar to those of proper bone, but in different proportions, the carbonate of lime preponderating. Thus the shells of crabs and lobsters contain from fifty to sixty per cent. of carbonate, and but from three to six of phosphate of lime, the rest being animal matter. Oyster-shells contain but a trace of animal matter, being almost pure carbonate of lime; and the substance termed cuttle-fish bone has the same composition nearly as crab-shells.

SECTION II.

OF THE COMPOSITION OF THE BLOOD, AND THE PHENOMENA OF RESPIRATION.

Blood is, in the higher classes of animals, an opaque, thick, red fluid; its specific gravity about 1·055; it has a salty and nauseous taste, and a peculiar smell, resembling that of the animal whence it had been derived.

When the blood of any red-blooded animal is allowed to rest, it gradually forms a soft jelly, from which, after some time, a thin yellowish fluid (serum) separates, while the red jelly or coagulum contracts in volume, and acquires greater consistence. If this *coagulation* of the blood takes place slowly, the upper portion of the coagulum becomes white or pale yellow, forming thus the *buffy coat.* There is no doubt that the blood, while in connexion with the animal, participates in its life, and the phenomena of coagulation are to be referred to a new arrangement of its materials consequent on the loss of that vitality.

The serum of the blood, when coagulation has been perfect, is of a yellowish, sometimes greenish colour; its taste is dull and salty; its specific gravity about 1·028; it is thick-fluid, like olive oil; when heated to 140°, it coagulates.

If we examine under the microscope the appearance presented by blood, we find that it consists of a great number of minute red particles swimming in a nearly colourless liquor. These red particles are flattened disks, in man and the mammalia round, in other animals elliptical. Their size is variable, being in man from $\frac{1}{4000}$th to $\frac{1}{8000}$th of an inch in diameter, but larger in most other animals. In the frog they are about $\frac{1}{1100}$th. They consist of a central colourless nodule, and an investing ring, which is coloured red by a material (*Hematosine*), which may be dissolved out without the constitution of the globule being otherwise essentially altered.

The blood contains a large quantity of *albumen*, partly dissolved, and remaining in the serum after coagulation, partly in a solid state, forming the great mass of the globules. In the living body the blood contains also *fibrine* in solution, but this separates soon after extraction from the body; it assumes a solid form, and investing, as a sponge, the red globules, forms with them the coagulum. The fibrine is thus the element active in the coagulation of the blood, the globules being but passively engaged in it. In addition to these essential organic elements, the blood contains a variety of salts, as common salt, phosphates of magnesia, ammonia, and lime, lactates of soda and magnesia. The best analyses of the blood are those by Lecanu, and the results for blood and serum are that they contain,

	Blood of Man.	Serum of Man.
Blood globules	13·30	
Fibrine	·21	
Albumen	6·51	8·12
Fatty substances	·37	·34
Extractive matters	·30	·46
Alkaline salts	·84	·75
Earthy salts	·21	·09
Water	78·02	90·10
Loss	·24	·14
	100·00	100·00

He found these proportions liable to fluctuation, and to vary according to the sex. The maxima and minima of each constituent which he found for the human subject of each sex were,

Constituents.	Male.		Female.	
	Max.	Min.	Max.	Min.
Water	80·5	73·2	84·84	75·00
Albumen	6·3	4·85	6·8	5·00
Globules	18·6	11·05	16·71	7·14
Fibrine	·4	·20	·31	·20

The fatty substance of the blood is a mixture of cholesterine with stearic and oleïc acids, and a peculiar fatty substance, termed *Seroline*, the history of which is yet incomplete, and which differs from cholesterine most in containing nitrogen. None of the phosphuretted fats of the brain appear to exist in blood.

The chemical history of fibrine and albumen having been already given, it remains only to describe the peculiar colouring matter, for the most accurate knowledge we possess concerning which we are indebted to Lecanu's elaborate researches on the blood. His method of preparing hematosine is as follows:

Blood, which has been freed from fibrine by beating with a twig, is to be mixed, with continual agitation, with sulphuric acid diluted with its own weight of water, until the whole mass solidifies to a brown pulp, from which the acid liquor is to be then drained off on filtering paper, and the last portions removed by washing with alcohol. The mass thus obtained, which is a mixture of sulphates of albumen and of hematosine, is to be boiled in successive portions of alcohol as long as this becomes brown. The liquors, being filtered when cold, are to be neutralized by ammonia, by which albumen and much sulphate of ammonia are precipitated, while a compound of hematosine and ammonia remains dissolved. This solution is to be then evaporated in a water-bath to dryness, and the residue washed with water, alcohol, and ether, to remove the salts and fatty matters which were contained in it. Being then redissolved in alcohol by means of ammonia, evaporated to dryness, and washed again with water, the hematosine remains pure, but in its coagulated form.

It is a dark brown mass, tasteless and inodorous; when heated, it does not melt, but swells up and evolves ammoniacal products; it is insoluble in water, alcohol, and ether; it forms with the mineral acids compounds which are insoluble in water, but soluble in alcohol. By caustic alkalies it is dissolved with a blood-red colour, and these combinations are soluble in water, alcohol, and ether. Hematosine contains neither phosphorus nor sulphur, but iron in large quantity (6·64 per cent.). By Mulder's analysis, the formula of hematosine is $C_{44}H_{22}N_3 . O_6Fe$. It hence has no connexion with proteïne or albumen. The state in which the iron exists

in hematosine has been, even up to the present day, an object of much discussion among chemists; but with the knowledge we now possess of hematosine in its pure form, we must consider the iron to be an integral part of its organic constitution, as sulphur is in albumen, or arsenic in alkarsine; and the opinion of its being oxidized, and combined with the true organic element as a kind of salt, can no longer be supported. If a solution of hematosine be acted on by chlorine gas, a white flocculent precipitate is produced, and the solution contains chloride of iron.

Although hematosine is the colouring material of the globules of the blood, it is present but in very small quantity; 100 parts of dried globules containing but from four to five of pure hematosine. In the blood globule, the hematosine is in its uncoagulated state, and possesses properties somewhat different from those of its coagulated form, as prepared by the process above given. A solution of the coloured blood globules in water, when exposed to the air, becomes of a brighter red colour, being thus partially arterialized. When evaporated at a temperature of 120°, it gives a dark red mass, which is completely soluble in cold water. Its solution coagulates at 155°, leaving the liquor clear yellow. It is coagulated also by alcohol and by acids. The hematosine then passes into the insoluble condition already described.

I have hitherto spoken of the colourless ingredient in the blood globules as being albumen, with which, indeed, it is almost identical in properties, but still differs in some points. It has been termed *Globuline.* In its uncoagulated condition it cannot be separated from hematosine, and is there distinguished from albumen principally by being insoluble even in a very dilute saline solution, which dissolves albumen readily. It is hence that the globules swim unaltered in the serum of the blood, but are readily dissolved by pure water. On this principle is founded a method of isolating the blood globules. If the blood, when extracted from the vein, be received in a vessel containing a solution of Glauber's salt, coagulation is prevented, as the fibrine remains dissolved, and by filtering the liquor so obtained, the serum and water pass off, and the globules remain mixed only with a little of the salt. The globuline cannot, however, be separated from the hematosine except by acids, which, as described in the preparation of hematosine, then combine with the globuline. Mulder found the organic element in the sulphate of globuline to have the composition of proteïne (see p. 666).

Alteration of the Blood in Disease.—The examination of the state of the blood in disease, although presenting important relations to pathology and to practice, has been hitherto conducted in a manner too disconnected and superficial to afford satisfactory results. This branch of chemical pathology has, however, been taken up by the illustrious Andral, who, in conjunction with M. Gavaret, has published the results of the analysis of the blood in 360 cases of disease, in a memoir, from whose publication may be dated the commencement of a true pathology of this fluid.

In the method which, by the advice of Dumas, they adopted, the quantity of fibrine, of globules, of the solid materials of the serum (which may be considered as albumen), and the quantity of water in each specimen of blood, were determined. The pure hematosine was not isolated, and the salts were considered as sufficiently important to necessitate their separation only in certain cases. As a point of comparison, they assume

as the standard of healthy blood, that 1000 parts contain 790 of water, 127 of globules, three of fibrine, and eighty of solid constituents of the serum, of which eight are inorganic; which numbers almost coincide with Lecanu's analysis, as already given. Their researches have enabled them to recognise four classes of diseases in which the composition of the blood is essentially altered, though in different ways.

The first class presents as a constant alteration *an increase in the quantity of fibrine;* it includes diseases remarkably different in their locality and form, but all belonging to the class of *acute inflammations.* In some cases of morbid deposition, as in tubercle and cancer, a similar increase in the quantity of fibrine is found, but it may be doubted whether it be due to the abnormal growth, or to the inflammatory action which accompanies it.

In the second class, the *fibrine remains stationary, or even diminishes in quantity, while the globules increase in proportion to the fibrine.* The diseases which belong to this class are *continued fevers without local inflammation,* and some form of *cerebral hæmorrhages.*

In the third class, the fibrine remaining unchanged, there is a remarkable *diminution in the quantity of the globules;* of these diseases *chlorosis* may be taken as the example; and in the fourth class, it is no longer the fibrine or globules which are the subject of the morbid change, but the quantity of *albumen in the serum is diminished.* Of this class of affections *Bright's disease* is the type.

Without entering into the details of these researches, which are excluded by the limited extent of this work, I shall merely present in the following table an example of the constitution of blood in each of these classes of morbid alteration.

Constituents.	Health.	1st Class.	2d Class.	3d Class.	4th Class.
Fibrine	3	7	2	3	3
Globules	127	125	136	47	82
Albumen . . .	72	78	69	75	58
Salts	8	7	7	8	7
Water	790	783	786	867	850

The appearance of albumen in the urine in Bright's disease is evidently connected with its diminution in the serum. The oily materials which are usually found in the blood, and the remarkable diminution which occurs, not so much in the globules as in the hematosine, had not attracted Andral's attention in the memoir now described. These oily substances are of the same nature as the proper fatty matters of the blood, but present in excessive quantity.

It has been observed that in *cholera* the blood becomes so thick as to arrest the circulation, and contains from thirty to forty-five per cent. of solid matter; it is then, also, less strongly alkaline than healthy blood. This is connected probably with the matters vomited and evacuated, which are strongly alkaline, and contain a quantity of albumen.

The blood has been found occasionally, in cases of *diabetes mellitus,* to contain traces of sugar; the great discordance of the results obtained may perhaps result from the sugar being contained in the blood only for a short time after meals, and then being rapidly evacuated by the kidneys. In *jaundice* the green colouring matter of the bile has been observed in the serum of the blood. Other observations of morbid constituents of the blood are too indefinite to justify me in occupying space

with them. The observation of Barruel, that, by heating the blood of any animal with a little oil of vitriol, the odour of the animal is so powerfully evolved as to be easily recognised, appears well founded, and may be useful in medico-legal questions, where, however, it should be employed with exceeding circumspection.

Of Respiration.—In the living body, the blood in the veins and arteries is well known to differ remarkably in colour, in the former being of a dark purple red, and in the latter of a bright vermilion colour. The change from the venous to the arterial state is effected during the passage of the blood through the capillary vessels of the lungs, where it is exposed to the action of an extensive surface of atmospheric air, while the arterial blood, in traversing the general capillary system of the body, assumes the dark red condition in which it is returned to the heart by the veins. Even out of the body, this change of colour is produced when venous blood is exposed to the air, especially if agitated therewith, and still more with pure oxygen; even the globules, when separated from the serum and dissolved in water, become brighter in colour, and partially arterialized by exposure to the air. Yet, although the vital properties of the blood depend essentially upon this change of colour, we are not yet able to connect it with any alteration in the composition of the constituents of the blood, or even in their relative proportions. Arterial and venous blood contain sensibly the same quantity of water, fibrine, globules, albumen, and salts; and, by analysis, the composition of these bodies is found to be identical, no matter what kind of blood they are derived from. To trace the difference of nature between arterial and venous blood, it is therefore necessary to study it under other points of view than its proximate or elementary composition, so far as we have yet examined it.

The air which has been employed in respiration is found to have undergone an important change of constitution; its volume is but slightly, if at all, altered; but a quantity of oxygen has disappeared, and is replaced by carbonic acid, in generally an equal volume. Air which has been once respired is found to contain from three to four per cent. of carbonic acid; and if the same quantity of air be continually breathed, the animal dies, with all symptoms of narcotic poisoning, when the carbonic acid has accumulated to from eight to ten per cent. The action of the air in expiration is therefore to remove carbon from the blood. The quantity so taken from the system in twenty-four hours is very large, and makes up the principal portion of that element which we take in with our food; yet such is the activity with which its assimilation proceeds, that no perceptible change in the solid elements of the blood can be detected.

It was at one time a much disputed point whether the carbon so separated from the system was directly secreted from the lungs, and burned off, as it were, by contact with the oxygen of the air, or whether the oxygen was first absorbed by the blood, and carried by the circulation to every portion of the body, where it combined with the carbon, which was there present in excess, and the carbonic acid so produced, being dissolved by the venous blood, was thrown off, on arriving at the surface of the atmosphere, in the lungs. The progress of science has, however, finally decided in favour of the latter view, to which the fullest confirmation has been given by the careful and elaborate experiments of Magnus.

He found that both arterial and venous blood hold dissolved quantities of gases, oxygen, nitrogen, and carbonic acid, which amount to from one tenth to one twentieth of the volume of the blood. The proportions of these gases to each other are different in arterial and venous blood; the oxygen in arterial blood being about one half of the carbonic acid, while in the venous blood it seldom amounts to more than one fifth. The difference is greatest in young animals, and probably is proportional to their activity of nutrition. The quantity of nitrogen appears to be the same in both kinds of blood, making from one fifth to one tenth of the gaseous mixture.

The physico-chemical conditions of respiration are simply explicable upon these results. By the principle of gaseous diffusion (p. 267), the fine lining pulmonary membrane being permeable to gases when the venous blood arrives at the surface of the lungs, a portion of the carbonic acid which it contains is evolved, and a quantity of oxygen gas absorbed in place of it. These two quantities are not necessarily equal at each moment, though ultimately they become so, and hence the volume of oxygen absorbed is generally, though not universally, equal to that of the carbonic acid given out. There appears, from the presence of nitrogen in equal quantity in both kinds of blood, to be an absorption and evolution of that gas, simply from physical laws, and independent of any direct application of it to the nutrition of the animal; hence the volume of nitrogen in air is sometimes increased, and at others diminished, by respiration, and an animal evolves much nitrogen when respiring an artificial atmosphere of oxygen and hydrogen, while Bousingault has shown the rate of nutrition of an animal to be proportional to the quantity of nitrogen it receives as food, and that none of that principle is really assimilated from the air.

It is still not by any means easy to decide upon the cause of the change of colour which occurs in the blood during respiration; for this should appear connected, not merely with the presence of certain gases in the blood, but upon a true change in the constitution of the hematosine, which analysis cannot direct. Stevens first directed attention to the remarkable influence which saline bodies have upon the colour of the blood. If dark venous blood be put in contact with a solution of common salt, Glauber's salt, nitre, or carbonate of soda, it becomes as vermilion-coloured as if it had been truly arterialized. On the contrary, the presence of carbonic acid impedes this action, and gives to blood, so reddened by a salt not in excess, the dark tint of venous blood. If we consider, therefore, the arterial tint to be due to the natural combination of the colouring matter with the saline constituents of the serum, this will be darkened when, by passing through the capillary system, the blood takes up an excess of carbonic acid; and again, in the lungs, when the carbonic acid is replaced by oxygen, the vermilion colour is restored, not by any active agency of the oxygen, but by the natural tint of saline hematosine becoming evident. Although this theory of the change of colour is by no means free from objections, it appears to me to be better founded than any other that has been proposed.

Animal Heat.—The phenomena of respiration consisting mainly in the conversion of carbon into carbonic acid by union with oxygen, the heat which is developed in the body of all red-blooded animals has been naturally referred to that source; and as we know that the change

from the arterial to the venous condition of the blood occurs at every point of the system, the almost complete equality of temperature throughout the body in health is explained. That the great source of heat is the respiratory process, is abundantly proved by the temperature being highest in those animals, and in the same animal at those periods when the circulation is most rapid, and the quantity of air consumed the greatest; but it has been calculated that the heat evolved by the combustion of the quantity of carbon thrown off from the body in twenty-four hours is not more than eight tenths of the quantity generated in the body during that time, and the origin of the remainder must be found in the action of the muscles and in the nervous power, which appears of itself to be a distinct source of animal heat.

SECTION III.

COMPOSITION OF THE DIGESTIVE ORGANS AND OF THEIR SECRETIONS. CHEMICAL PHENOMENA OF DIGESTION.

Mucus.—The lining membrane of the alimentary canal is moistened with a liquid possessing many characters of the vegetable mucus (tragacanthine, p. 530), but containing nitrogen. It is a thick tenacious substance, which contains, dissolved in the water through which it is diffused, the ordinary salts of the serum of the blood; it swells up with water to a considerable mass, but without dissolving; it dissolves in alkaline liquors, and is precipitated therefrom on the addition of an acid and by tincture of galls; the mucus from different parts of the mucous membrane is, however, by no means identical in properties.

The liquid secreted by the internal surface of the stomach, *the Gastric Juice*, which exercises an important influence on digestion, differs essentially in its characters from mucus. When the stomach is empty and contracted, it contains only ordinary mucus; but if even indigestible substances be introduced, and still more after taking proper food, a liquid is abundantly poured out, which is colourless or very pale yellow, and contains a very small quantity of solid matter (two per cent.), which consists principally of inorganic salts (common salt and sal ammoniac, with a trace of a salt of iron); it is specially characterized by the presence of a notable quantity of free muriatic acid, the proportions of which appear to vary with the activity of the digestive powers at the time. This gastric juice possesses the remarkable property of softening down and dissolving fibrine and albumen, and thus converts the masses of food into the uniform pulp (*Chyme*), from which the absorbing vessels of the small intestines take up the nutritious elements.

If we form an artificial gastric juice by mixing together the muriatic acid and salts in the proper proportions, it is found to be totally incapable of dissolving the materials of the food, and, indeed, to be quite inactive towards digestion. The organic material of the gastric juice, although its quantity be so minute, is therefore essential to its powers, and these may be perfectly conferred upon the previously inactive artificial juice by the addition of a little of the mucus of the stomach, or by steeping in the acid liquor, for a short time, a small portion of a mucous membrane, and filtering the liquor. For this purpose it is not even necessary to use the mucous membrane of the stomach, for that of the bladder has been found to act equally well. The substance which is dissolved out of the membrane in these cases has been termed *Pepsine.* It has not been obtained in a

truly isolated or pure form, but its properties are very remarkable. For its full activity it requires the presence of a free acid, as the artificial gastric juice becomes much less active in dissolving food, when neutralized by an alkali, though it retains other properties, as that of coagulating milk like rennet. If the artificial gastric juice be precipitated by acetate of lead, the precipitate washed, and then decomposed by sulphuret of hydrogen, the solution thus obtained possesses all the digestive powers of the juice. Hence the pepsine and muriatic acid act together in combining with oxide of lead. The process given by Schwann for preparing the best artificial gastric juice, is to mix water with $2\frac{3}{4}$ per cent. of muriatic acid, of specific gravity 1·13, and digest therein the mucous membrane of a stomach for twenty-four hours, then to filter.

Pepsine appears to be completely decomposed by contact with alcohol, or by the heat of boiling water. Its powers are destroyed, also, by deoxidizing substances. The solution of albumen and fibrine in gastric juice is essentially different from their solution in muriatic acid, as in the former case the quantity of acid is very minute in relation to the quantity of material dissolved, and after solution the acid still remains quite uncombined.

Fremy has discovered that the peculiar fermentative process, which sometimes spoils the manufacture of sugar, and which I have described (p. 536) as the mucous fermentation, is capable of being induced by contact with mucous membrane (by pepsine ?). He has found that sugar of milk may thus be converted to an unlimited extent into lactic acid, no other product appearing. The vegetable ferments are able to produce the same effect, but in a different stage of decomposition from that in which they induce the saccharine or alcoholic fermentations.

The action of the stomach in digestion appears, therefore, to be, so far as our actual knowledge extends, a purely catalytic fermentative action; one in which the active excitant is an organic substance (*Pepsine*) secreted by the mucous surface, and whose properties are developed by the presence of muriatic acid, which is secreted at the same time. The new products into which the food, fibrine, albumen, gluten, starch, oils, sugar, &c., are converted, and which collectively constitute the white uniform pulp termed by physiologists *Chyme*, have not been made the subject of accurate chemical research.

In the mouth the mass of nutritive material is acted on by a liquid which is secreted by the salivary glands, the *Saliva*. It is alkaline, and holds in solution not one per cent. of solid matter, which contains some carbonate of soda and common salt, admixed mucus, a trace of sulphocyanide of potassium, and a peculiar organic body termed by Tiedemann and Gmelin *Salivary Matter*. This last substance is soluble in water; its solution is not coagulated by heat, nor precipitated by tincture of galls, corrosive sublimate, acetate of lead, nor by acids. The pancreas, though so similar in structure to the salivary glands, has a different secretion; it contains no salivary matter, nor any sulphocyanide of potassium, but albumen and some salts; it is generally slightly acid.

Composition of the Bile.—The precise part which this remarkable secretion performs in the animal economy is not yet fully known. It has been the subject of repeated and accurate chemical examination, although, from the facility with which its elements are transformed into other bodies, by the action of the reagents employed, every succeeding

analysis has led to different results. I shall only notice the late researches of Gmelin, Demarçay, and Berzelius.

In the elaborate work on digestion, undertaken in conjunction with Tiedemann, Gmelin analyzed principally the bile of the ox, from which, however, as far as observations have been made, human bile does not appear essentially to differ. He obtained from it a volatile body having the odour of musk, cholesterine, margaric and oleïc acids, a peculiar acid, the *Cholic Acid;* colouring matters, *Biliary Resin, Biliary Sugar, Taurine,* a glutinous substance, caseüm, salivary matter, ozmazome, and a number of salts of organic and inorganic acids. Demarçay looks upon all of these substances as being produced by the reactions used, and denies that any of them really exist in the bile. He considers the bile to be a soda-soap of a peculiar fatty acid, the *Choleïc Acid,* that is, a *Choleäte of Soda.* The choleïc acid is obtained by dissolving one part of the alcoholic extract of ox-gall in 100 parts of water, and mixing the solution with two parts of sulphuric acid diluted with ten of water. By gradual evaporation of the liquor, oily drops separate. It is to be then cooled, and these drops, which are common fat, removed. On then standing for eight or ten hours, the choleïc acid gradually separates, and, being digested with ether to remove some adhering fat, is pure. It is a brittle yellow-white mass, tastes bitter, softens by a heat of 250°, but does not really melt; it is slightly soluble in water, but abundantly in alcohol and ether. It forms, with bases, salts which do not crystallize; its formula was found to be $C_{42}H_{36} . N.O_{12}$.

When the alcoholic extract of the gall is boiled for a long time in contact with an excess of muriatic acid, the choleïc acid is decomposed, and the most remarkable products are the *Taurine* of Gmelin, and a new acid, the *Choloïdic Acid.* The latter is a fatty acid, not volatile, yellow, of a bitter taste; it forms a soft mass with warm water, but without dissolving; it dissolves readily in alcohol and ether, and these solutions redden litmus. By Dumas's analysis the formula of this body appears to be $C_{38} H_{30}O_7$. It does not contain nitrogen. The *Taurine,* which remains in the acid liquor from which the choloïdic acid separates, is obtained by evaporation, and mixing with alcohol, from which solution it crystallizes gradually in six-sided prisms, which are perfectly neutral; it fuses and is decomposed by a strong heat; it dissolves in twelve and a half parts of cold, and in less of boiling water, but requires 573 parts of spirit of wine for solution; it is scarcely acted on even by the strongest acids, and is not precipitated by any metallic salt; its formula is remarkable, being $C_4H_7 . N.O_{10}$, including the elements of binoxalate of ammonia and 2 Aq.

If the bile be treated with an excess of a strong alkali, the choleïc acid is totally broken up into ammonia and the *Cholic Acid* of Gmelin. It crystallizes from its hot aqueous solution in delicate silky needles, of a brilliant white colour; its taste is at once acid and sweet; by heat it is melted and decomposed; it is very slightly soluble in water, but copiously in alcohol; its solutions redden litmus; it contains no azote; its formula being, as determined by Dumas, $C_{42}H_{36}O_{10}$.

Demarçay's examination of the bile appears thus quite satisfactory in showing that the cholic acid and the taurine are secondary products, and he considered the other substances found by Gmelin to be choleïc or choloïdic acids in an impure form. But Berzelius, who has been occupied in the re-examination of the subject, has decided that the choleïc acid of

Demarçay is really the body which is impure, being a mixture of the true biliary substance (*Bilin*, Gmelin's *Biliary Sugar*) with the biliary resins. He found that when the alcoholic extract of the bile is mixed with sulphuric acid, no precipitate appears for a considerable time, showing that the substance, which really exists in the bile combined with soda, is completely soluble in water, and it is only by its gradual change that the precipitate (choleïc acid) occurs. By digesting this substance with ether, he removed from it a resin, which, by possessing acid properties, and by means of combination with barytes, is shown to be a mixture of two distinct acid resins, *Fellic Acid* and *Cholinic Acid.* The material insoluble in ether is the true *Bilin;* it is not acid, of a bitter taste, soluble in alcohol and water in all proportions, but insoluble in ether; when heated, it becomes soft, and burns like a resin; its watery solution is rapidly decomposed, especially if warmed; by contact with acids or alkalies, it is immediately changed in constitution: the substances produced are different, according as the degree of alteration is more or less advanced. Those more important are the following:

The *Biliary Matter*, which is the state in which the greater part of the bilin exists in ordinary bile, being the first product of its decomposition, is a white, bitter substance, which has a marked acid reaction, and is decomposed by oxide of lead into bilin and *Bilifellmic Acid*, which is the choleïc acid of Demarçay. The formation of taurine is accompanied by that of another body, *Dyslysin*, which is a colourless resinous substance, very sparingly soluble in water. The fellinic and cholinic acid have been noticed above.

When the bile has been kept for a long time, it is decomposed by a kind of fermentation, and two acids formed, termed the *Fellanic* and *Cholanic Acids:* they are white earthy powders sparingly soluble in water; the former melts only far above 212°; the latter is very easily fusible.

The Colouring Matter of the Bile is present during health in but small quantity, but in disease it sometimes accumulates so as to produce solid masses. When pure, it is a reddish-yellow powder, which is scarcely soluble in water or in alcohol, but dissolves easily in solution of caustic potash. This solution is of a clear yellow colour, but when exposed to the air it becomes deep green, absorbing oxygen. This change is remarkably produced by nitric acid, and it is indeed the reaction by which the presence of the bile in the serum of the blood, in the urine, in the skin and eyes, &c., may be shown in cases of jaundice. If too much nitric acid be not added at once, the yellow liquor becomes at first green, then blue, violet, and finally red, all these changes occurring in a few seconds. After a moment the red colour also disappears, the solution becomes yellow, and the colouring matter is found to be totally decomposed. The solution of the colouring matter in potash is precipitated by muriatic acid in deep green flocculi, which dissolve in nitric acid with the effect already noticed, and are soluble in caustic ammonia and potash, with a rich emerald-green colour. These reactions show that, by a process of oxidizement from the original yellow substance, green and red materials may be generated, in which forms the colouring matter exists naturally in various animals, according as their bile is yellow, green, or reddish, and also gives rise to the concretions of various kinds that are deposited in disease. The most common kind of gallstone consists, however, of cholesterine.

This yellow material Berzelius names *Bilifulvin.* He considers the green colouring matter present in healthy bile to be identical with chlorophyll (p. 621).

The bile contains generally about nine per cent. of solid matter; but in the present state of our knowledge of its constituents, it is evidently impossible to assign the numerical proportions in which they exist.

The substance found in the bile, and termed *Erythrogen* by Bizio, is too apocryphal to require any notice.

The examination of the farther processes of digestion involves considerations too purely physiological to be entered into.

Chyle and Lymph.—The nutritive materials extracted from the food by the absorbing vessels of the intestine is thrown into the thoracic duct, where it meets with another fluid, which is transmitted to the same vessel from all parts of the body by the colourless veins or lymphatics. The fluid from the intestines is termed *Chyle*, that from the body generally is termed *Lymph.* It is the mixture of these that alone has been examined, for the vessels which carry either separately are too minute to allow of the extraction of their contents in a pure form.

When taken from the thoracic duct a few hours after a meal, when, probably, the chylous element prevails, it is a whitish, opaque liquid like milk, with generally a reddish shade; a short time after separation from the body it coagulates; the clot is at first pale, but it soon becomes light cinnabar red; the milkiness of the serum is due to the presence of oil; it contains albumen, and coagulates by heat. Except that it is more dilute, and that the hematosine is for the most part absent (not yet formed), the chyle and lymph have the same composition as the blood. It appears to vary, however, with the nature of the food, as Dr. Prout found the chyle of dogs fed on vegetables to contain a much smaller quantity of albumen than when they had had animal food. Dr. Prout also indicates in chyle the existence of a substance which he terms *Incipient Albumen*, which is not coagulated by heat, except after the addition of acetic acid. The properties of this form of albumen, however, are not fully known. The results of their analyses of chyle are here given; that by Berzelius was the chyle of a horse, killed some time after having fed abundantly with oats; and of those by Dr. Prout, No. 1 was from a dog supported on vegetable, and No. 2 of a dog supported on animal food. 100 parts contained,

Berzelius.	
Dry Clot	0·78
Albumen	4·49
Fatty matters	1·67
Extractive matters and salts	1·44
Water	91·62

Prout.	No. 1.	No. 2
Fibrine	0·6	0·8
Incipient Albumen	4·6	4·7
Albumen	0·4	4·6
Oil and Sugar	trace	trace
Salts	0·8	0·7
Water	93·6	89·2

SECTION IV.

CONSTITUTION OF THE URINE IN HEALTH AND IN DISEASE.

The nature of this secretion has at all periods been an object of considerable interest to the physician and to the chemist, from the indications which changes in its composition give of disease of important organs, and from the number and interest of the organic substances it contains. As in almost all other branches of animal chemistry, Berzelius first determined accurately its constitution, and lately Lecanu has ascer-

tained with great care the limits to which the proportions of its ingredients may vary in health, and thus established a correct basis of comparison for urine in the various conditions of disease.

The specific gravity of urine varies from 1016 to 1030. In general, if the excretion exceeds in quantity thirty-two ounces in twenty-four hours, the specific gravity falls proportionally below 1030; but if the quantity be under thirty-two ounces, the specific gravity for a man in active health is generally 1030, but less for women. The important organic constituents of the urine are *Urea* and *Uric Acid*, which will require a detailed and special examination; the other principles, though numerous, being of less moment, need be only noticed in the following statement of Berzelius's general analysis of the urine. He found 100 parts to contain,

Water	933·00	100·00
Urea	30·10	
Free lactic acid, lactate of ammonia, and animal extract	17·14	
Uric acid	1·00	
Mucus of the bladder	0·32	
Sulphates of potash and soda	6·87	
Phosphates of soda and ammonia	4·59	
Common salt	4·45	
Sal ammoniac	1·50	
Phosphates of lime and magnesia	1·00	
Silica	0·03	

Urea.—$N_2C_2 . O_2H_4$ or Ur. Eq. 60 or 750.

The artificial formation of this remarkable substance in various ways, has been noticed already in many places (as 511, 515). It may be obtained from urine by evaporation to the consistence of a thick sirup in a water-bath, and mixing the mass remaining with three times its volume of nitric acid, specific gravity about 1·25, which had been perfectly freed from all traces of nitrous acid which it might contain, as this last instantly decomposes urea. The liquor forms a crystalline pulp, which, being kept carefully cool, may be freed from the liquor by draining and pressure between folds of paper. The impure crystallized nitrate of urea thus obtained is to be dissolved in a small quantity of boiling water, and recrystallized by cooling. These crystals being again dissolved in water, are to be digested with animal charcoal to remove the colouring matter, and then with an excess of carbonate of lead, until completely neutral. The solution so obtained, being evaporated very carefully in a water-bath to dryness, is to be treated with boiling alcohol, and filtered. The pure urea separates from the alcoholic solution, on cooling, in brilliant white four-sided prisms.

Urea is much more simply and economically obtained by the transformation of cyanate of ammonia, for which purpose the process given by Liebig answers best.

An impure cyanate of potash is prepared by roasting yellow prussiate of potash (as described p. 515), and this is mixed with a solution of sulphate of ammonia in water, and the whole then boiled with alcohol, which dissolves out urea, and leaves the sulphate of potash undissolved. On cooling, the urea crystallizes, and may be obtained quite pure by another crystallization from alcohol.

The taste of urea is fresh like nitre; its reaction is quite neutral; it is inodorous. When heated to 220°, it melts, and at a higher tempera-

ture is decomposed, giving carbonic and cyanuric acids and ammonia. It dissolves in less than its own weight of water at 60°, producing great cold; it is soluble in much less boiling water. If the urea be quite pure, its solution remains for a long time unaltered; but if it contains any traces of an azotized substance which putrefies, this acts as a ferment, and the decomposition extending to the urea, this assimilates the elements of water, and is totally converted into carbonate of ammonia, $N\,C_2 \,.\, O_2H_4$ and H_4O_4 producing $2(C.O + N.H_4O.)$. It is this decomposition that renders urine alkaline in a few hours, generally, after it is voided. Urea dissolves in five parts of cold and one of boiling alcohol. In ether it is almost insoluble.

In contact with strong acids, urea is decomposed, giving off carbonic acid, and forming an ammoniacal salt. When the acids are dilute, it unites with them, although without neutralizing them, and forms crystalline compounds, of which but a few have been accurately examined. The oxygen salts of urea resemble those of the vegetable alkalies, melamine, ammonia, &c., in containing an atom of associated water.

Nitrate of Urea ($Ur.H.O. + N.O_5$) crystallizes in large brilliant plates by the cooling of its solution. It is pleasantly acid, and is soluble in alcohol, but much more so in water; if heated rapidly, it explodes. It is sparingly soluble in dilute nitric acid, whence the addition of a great excess of nitric acid serves as a test for the presence of urea, this salt being precipitated in bright pearly scales.

Oxalate of Urea ($Ur.H.O. + C_2O_3$) crystallizes in long rhomboidal tables. It tastes acid; it is copiously soluble in boiling water, but crystallizes almost completely out on cooling, as 100 of water retain but 4 of the salt. It is still less soluble in alcohol.

Lactate of Urea crystallizes in fine plates and needles; it is very soluble. There is reason to consider that the urea is naturally combined with lactic acid in the urine. The other salts of urea are not important.

The quantity of urea secreted in health appears pretty regular in the same individual, when the diet remains the same, and not to depend upon the quantity of liquor excreted. It varies, however, very much in different individuals, and is much more abundant in men in active age than in women or in old men. Thus Lecanu found the quantity of urea secreted in twenty-four hours, by men in the prime of age, to vary from 350 to 500 grains; in women it varies from 150 to 430 grains; while with old men the limits were 80 and 180 grains. In children the quantity is still smaller, and infants secrete scarcely a trace of urea.

Uric Acid, and the Bodies derived from it.

The uric acid exists in the urine of all carnivorous animals. In birds, reptiles, and many insects, it is voided with the excrements, and the urine is in such a state of concentration as to form a white mass, nearly solid, which consists almost totally of urate of ammonia. In the small islands of the South Sea, which are inhabited by great flocks of aquatic birds, it accumulates in such quantity as to be an article of commerce, being brought to South America, and even to Europe, under the name of *guano*, and used as manure. In many diseases it is generated by the system in abnormal quantity, and constitutes, free or combined with bases, the gouty and arthritic concretions, and many forms of vesical calculus.

For the purposes of the chemist, the uric acid is most easily obtained

from the white solid excrements of the larger serpents in the menageries. This is to be boiled in a solution of caustic potash, and the filtered liquor decomposed by the addition of muriatic acid in excess. The precipitate should be boiled in water for some time, then well washed and dried. It crystallizes in minute brilliant white scales, which are very slightly soluble in boiling water; the solution reddens litmus; it is tasteless; it dissolves in oil of vitriol, forming a crystallizable compound, which is decomposed on the addition of water: the action of nitric acid is different. When heated, it is decomposed, giving a great variety of products, urea, hydrocyanic and cyanuric acids, carbonate of ammonia, &c. Its formula is $N_4C_{10} . H_4O_6$; its salts are not well characterized; those of the alkalies are very sparingly soluble, and are decomposed by all acids except the carbonic acid. The *Urate of Ammonia* is the material of the white excrement (dry urine) of birds and serpents. The *Urate of Soda* is the principal material of gouty deposites. The uric acid is specially interesting for the number of important bodies to which it gives origin by the action of reagents, and of which some are also products of the organization; for our accurate knowledge of these we are indebted to the recent investigations of Liebig and Wöhler.

Allantoïn.—This substance exists in the waters of the allantoïs of the cow, being contained in the urine of the fœtus, from which it may be extracted by evaporation and crystallization. It is, however, much more easily formed from uric acid. Freshly-prepared peroxide of lead is to be added to uric acid, diffused through twenty parts of boiling water as long as its colour is destroyed. The boiling liquor is to be filtered, evaporated till crystals begin to form, and then allowed to cool. The allantoïn crystallizes, and the mother liquor contains abundance of urea. At the same time, oxalate of the protoxide of lead is produced, $2(N_4C_{10} . H_4O_6)$ and $5H.O.$ with $4Pb.O_2$, producing $4(C_2O_3+Pb.O.)$; with urea, $2(N_2C_2 . H_4O_2)$, and allantoïn, $N_4C_8 . H_5O_5$. On this reaction Liebig founds a theory of the constitution of uric acid, to which I shall have occasion again to recur. He considers it to contain urea ready formed, and a hypothetic substance, for which he proposes the names of *Uril*, or *Cyanoxalic Acid*, it being oxalic acid in which oxygen is replaced by cyanogen, C_2O_2+Cy. Thus uric acid, $N_4C_{10} . H_4O_6=N_2C_2 . H_4O_2+2(C_2O_2Cy.)$. In forming allantoïn on this view, the urea is set free, and the cyanoxalic acid, with oxygen and water, gives oxalic acid and allantoïn.

Allantoïn forms rhombic prisms, which contain an atom of water. It is sparingly soluble in water, and perfectly neutral. By boiling with a strong alkali, it combines with the elements of water, giving oxalic acid and ammonia. It does not form a definite compound with any base but oxide of silver.

Alloxan.—The products of the action of nitric acid on uric acid present considerable interest, from their number and connexion. On adding one part of uric acid gradually to four parts of strong nitric acid, it is dissolved with much heat, and copious disengagement of carbonic acid and nitrogen. The rise of temperature being prevented as much as possible, the liquor solidifies on cooling to a mass of granular crystals, which are to be drained, and then recrystallized from the smallest possible quantity of boiling water. This is *Alloxan;* its crystals are short right rhombic prisms, brilliant and colourless. In dry air they effloresce, losing 6 Aq.; at a higher temperature it crystallizes in oblique rhombic prisms which are anhydrous, and have the formula $N_2C_8 . H_4O_{10}$; its solution in water reddens litmus, and stains the skin purple; when neutralized by an alkali, it strikes an indigo-blue colour with a protosalt of iron; it is decomposed by almost all reagents, producing a series of bodies that will be successively examined; its origin consists, probably, in the uryl being

oxidized by oxygen from the nitric acid, leaving hyponitrous acid, which, reacting on the urea, gives the mixture of the carbonic acid and nitrogen gases. The alloxan may thus be considered as a hydrated deutoxide of uryl.

Alloxanic Acid is formed by acting on alloxan with strong alkalies or by barytes; when separated from its combinations by a stronger acid, it crystallizes in colourless needles, which have a strong acid reaction; its alkaline salts are soluble; those with the earths and heavy metallic oxides sparingly soluble; it is insoluble in water; its formula is $N_2C_8 . H_2O_8$ when dry, the alloxan having lost the elements of two atoms of water. When a solution of alloxanate of barytes is boiled, or when a solution of alloxan is gradually added to a boiling solution of sugar of lead, another acid is formed, *Mesoxalic Acid*, which in the latter case precipitates an insoluble salt of lead, and the liquor contains urea; the alloxan breaking up into $N_2C_2 . H_4O_2$ and $2C_3O_4$, which is the constitution of the mesoxalic acid, which has probably, therefore, an isomeric oxide of carbon (C_3O_3) for its base, and belongs to the same group as the mellitic and rhodizonic acids (p. 496). By oxidizing agents, the mesoxalic acid is converted into carbonic acid; thus, with a solution of nitrate of silver, it gives a clear yellow precipitate, which, when boiled, is converted into carbonic acid and metallic silver.

Mycomelinic Acid.—If a solution of alloxan in water of ammonia be heated, a brownish-yellow precipitate falls, which is mycomelinate of ammonia, by boiling which, or by washing with dilute sulphuric acid, the ammonia is removed, and the mycomelinic acid remains as a yellow jelly, which dries to a coarse yellow powder. It is sparingly soluble in water; its salts are gelatinous, sparingly soluble flocks; the formula of the acid is $N_4C_8 . H_5O_5$, being isomeric with anhydrous allantoïn.

Parabanic Acid.—If alloxan be heated with an excess of nitric acid, it dissolves, nitrogen gas is evolved, and, on cooling, the new acid separates; it is also easily procured from uric acid by using an excess of nitric acid; it forms colourless, transparent, six-sided prisms, and tastes like oxalic acid. It is partly volatilized and partly decomposed by heat. If the crystals be heated to 212°, they assume a reddish colour; the formula of the crystallized acid is $N_2C_6O_4+2$ Aq.; hence alloxan with 2O. produces $2C.O_2$, with 4H.O. and $N_2C_6O_4$. By contact with bases, this acid is decomposed, producing the *Oxaluric Acid.* This is best prepared by dissolving parabanic acid in caustic ammonia, boiling, and then letting the liquor cool; it forms a mass of small brilliant white crystals of oxalurate of ammonia. The oxaluric acid is also a product of other reactions on uric acid, some of which will be specially noticed hereafter. It is a strong acid, and is obtained free by dissolving its ammonia salt in boiling water, adding an excess of dilute muriatic acid, and rapidly cooling, when the oxaluric acid separates as a white or slightly yellow powder; if long boiled in water, it is decomposed into oxalic acid and oxalate of urea, of which it contains the elements, its formula being $N_2C_6 . H_3O_7+$Aq.

Thionuric Acid.—If sulphurous acid gas be passed through a saturated solution of alloxan until the liquor begins to smell strongly of the gas, and then ammonia be added in excess, after some time brilliant white rhombic tables form, which are thionurate of ammonia. By recrystallization, this salt generally becomes pale rose-red, but is not altered in constitution. To obtain the acid free, a solution of this ammonia salt is to be precipitated by acetate of lead, and the thionurate of lead decomposed by sulphuretted hydrogen. By evaporation of the liquor, the acid remains as a white semicrystalline mass; it is easily soluble in water, reddens litmus strongly; its formula is $N_3C_8 . H_7O_{14}S_2$: it contains thus the elements of one atom of alloxan, one of ammonia, and two of sulphurous acid; it is a bibasic acid. If a strong solution of thionuric acid be boiled, it becomes turbid, and soon solidifies to a mass of brilliant silky crystals, while the liquor contains much sulphuric acid; the crystalline substance being drained and washed with cold water, in which it scarcely dissolves, is termed *Uramil;* it is white, soluble in dilute alkaline liquors, and precipitated therefrom unchanged by the addition of an acid, but by strong alkalies it is decomposed, ammonia being evolved, and uramilic acid formed. The formula of uramil is $N_3C_8 . H_5O_6$; the thionuric acid might be considered as bisulphate of uramil. The *Uramilic Acid* is formed by the action of acids and alkalies on uramil; it crystallizes in colourless needles, which dissolve in acids and alkalies, forming with the latter well-defined salts; its formula is $N_5C_{16} . H_{10}O_{15}$.

Alloxantine.—This substance is formed as a product of the moderate oxidation of uric acid, or it may be obtained by acting on alloxan with deoxidizing agents. Uric acid is to be diffused through boiling water, and the dilute nitric acid added until a perfect solution is obtained. On filtering and cooling, the alloxantine gradually crystallizes. The mother liquor contains much urea. If sulphuretted hydrogen gas has been passed through a solution of alloxan, sulphur is deposited, and alloxantine formed, and the same effect is produced by acidulating the solution of al-

loxan, and immersing therein a slip of zinc; the alloxan is deoxidized by the nascent hydrogen. By the galvanic battery alloxan is resolved into oxygen and alloxantine. It is sparingly soluble in cold, but much more in boiling water, and crystallizes in short oblique rhombic prisms which contain 3 Aq., which they lose only by a heat above 300°. The solution of alloxantine reddens litmus, but does not form salts with bases, being immediately decomposed by contact with them. Its formula is $N_2C_8 . H_5O_{10}$

By oxidizing bodies, as nitric acid, chlorine, or oxide of silver, it is immediately converted into alloxan. If treated by an excess of sulphuretted hydrogen, more sulphur is set free, and the liquor becomes strongly acid. The body thus formed, if mixed with alloxan, regenerates alloxantine from both. If neutralized by carbonate of ammonia, a white crystalline precipitate forms, which is a salt of ammonia, of which the formula is $N_3C_8 . H_7O_8$. Liebig considers it to contain a body which he terms the *Dialuric Acid*, the formula of which is $N_2C_8O_4$, being isomeric with the cyanoxalic acid or uryl already noticed. The *Dialurate of Ammonia* is therefore $N_2C_8O_4+N.H_4O.+3$ Aq. It may be produced by adding hydrosulphuret of ammonia to a saturated solution of uric acid in dilute nitric acid, or by acting on alloxan with zinc and muriatic acid in excess. Though white when first produced, it becomes rose-red by drying, and at 212° blood-red, and loses ammonia. It is by no means established that this body is a true ammoniacal salt as described by Liebig, or that the dialuric acid really exists. Berzelius looks upon it as a compound of alloxantine and alloxantine-amide.

By boiling with sal ammoniac, alloxantine is converted into uramil and alloxan, while muriatic acid becomes free. By the action of oxygen upon an ammoniacal solution of alloxantine, uramil, oxaluric acid, and mycomelinic acid are generated.

Murexid.—This remarkable substance may be produced by a variety of reactions, none of which are, however, quite constant in their result. On evaporating a solution of uric acid in very dilute nitric acid until the liquor becomes flesh-red, and then adding dilute water of ammonia in slight excess, and cooling, the murexid crystallizes. In this process a very slight excess or deficiency of any of the ingredients prevents success, and Gregory proposes, as the most certain method, to dissolve four parts of alloxantine and seven of hydrated alloxan in 240 parts of boiling water and eighty of solution of carbonate of ammonia, when the murexid crystallizes by gradual cooling. By the action of uramil and ammonia it may also be generated, and is the ordinary source of the purple colours that are produced in many of the reactions already described.

The *Murexid*, the name of which is derived from the *murex*, the shell-fish furnishing the Tyrian purple, crystallizes in short rhombic prisms of a garnet-red colour, and by reflected light have a green metallic lustre. It dissolves sparingly in cold, copiously in boiling water; it is insoluble in ether and alcohol. Gregory has found that it is sometimes soluble, and at others insoluble in water of ammonia, whence he suggests that two different bodies have been confounded under this name. It dissolves in caustic potash, with an indigo blue colour, which disappears by heat, ammonia being evolved; it does not appear to combine with bases; its formula is $N_5C_{12} . H_6O_8$. By the mineral acids and by sulphuretted hydrogen it is decomposed, ammonia, alloxantine, alloxan, and dialuric acid being evolved, besides another body termed *Murexan.* This substance is more abundantly produced by dissolving murexid in a boiling solution of potash, and when the blue colour has totally disappeared, adding sulphuric acid in excess. It precipitates in white silky crystalline scales; its formula is $N_2C_6 . H_4O_5$; it dissolves in caustic alkalies without neutralizing them. If its solution in ammonia be exposed to the air, oxygen is absorbed and murexid regenerated.

The murexid was long since described by Prout under the name of *Purpurate of Ammonia;* and Fritzsche has revived the idea that it is really an ammoniacal salt of a distinct acid, *Purpuric Acid.* By the double decomposition of murexid with salts of potash, barytes, lead, and silver, he has obtained purpurates of these bases, the formula of which shows the acid to be composed of $N_5C_{16} . H_4O_{10}$. The murexid is, according to this chemist, composed of $N_6C_{16} . H_8O_{11}=N_5C_{16} . H_4O_{10}+N.H_4O$. The evidence brought forward by Fritzsche against Liebig's view is very strong.

In the urine of herbivorous animals, and occasionally in children, the uric acid is replaced by a different body, the *Hippuric Acid*, which exists therein combined with soda. The urine of horses and cows is to be evaporated to one eighth of its volume, and mixed with muriatic acid, which produces, after some time, a yellowish crystalline precipitate. This is to be dissolved by boiling with some lime; chloride of lime is to be added to the liquor until it is nearly decolorized, and the smell of urine has disappeared; being then digested with ivory black and filtered, the pure acid is

separated by muriatic acid. By the cooling of the liquor it crystallizes in delicate silky needles or rhombic prisms; its taste is very slightly bitter, but it reddens litmus strongly. When heated, it melts, and is then decomposed, giving a crystalline sublimate of benzoic acid with ammonia and prussic acid. It is very sparingly soluble in cold, but copiously in boiling water; very soluble in alcohol. By nitric acid and other oxidizing agents, it is decomposed, and benzoic acid is formed. Its salts are all soluble and crystallize; they resemble the benzoates exactly. The formula of the crystallized acid is $N.C_{18}.H_8O_5+Aq$. The constant transformation of this acid into benzoic acid has given origin to many theories of its constitution. It has been supposed by some to contain benzoic acid ready formed, by others benzamid, and by others oil of bitter almonds, but none of these views have even much probability in their favour.

Of the Urine in Disease. Urinary Calculi.

To the pathologist and physician, the indications of disease of the urinary and digestive organs, furnished by changes in the composition of the urine, are most valuable. The majority of the substances which are taken into the circulation, but are incapable of assimilation to our organs, are thrown off by this secretion, and hence a variety of medicinal substances may be traced to it after having been ingested, sometimes quite unaltered, at others modified in their nature. Thus, if alkaline salts of organic acids be taken into the stomach, the organic material is oxidized, probably during the action of respiration, while the alkali passes into the urine in the state of carbonate. If, however, the organic acid be taken uncombined, it escapes decomposition, and, passing into the urine, produces an abundant precipitate of salts of lime, in the case of the tartaric and oxalic acids.

Iodide of potassium and iodine pass into the urine, the latter as hydriodic acid. Some organic bodies, as asparagine and oil of turpentine, are decomposed, and the products which they form are excreted, giving to the urine peculiar odours, in the latter case like that of violets. Nitrate of potash, yellow prussiate of potash, and most other alkaline and earthy salts, pass into the urine unchanged. The majority of colouring matters are thrown out of the system by means of this secretion, while others, as cochineal and litmus, are not so given off.

The mineral acids, alcohol, camphor, most metallic salts, do not pass into the urine in any sensible degree.

Urine in Diabetes.—The most remarkable change in the nature of the urine occurs in diabetes mellitus. It is voided in great quantity. Its specific gravity is very high, from 1030 to 1050, and it is found to contain a very large quantity of grape-sugar, and very little urea. It was supposed that, in this disease, urea ceased to be formed by the system, and was replaced by sugar; but I have shown that, although the quantity of urea is very small in any one specimen of the urine, yet the total quantity is so much increased, that in twenty-four hours the natural quantity of urea is secreted; the secretion of sugar being an act of faulty digestion, and totally unconnected with the urea. These results have been fully confirmed by Macgregor. The diabetic urine sometimes contains albumen, which arises from complication of other forms of disease.

As the average composition of urine in diabetes, the following may be taken, analyzed by myself. Its specific gravity was 1·0363; it contained in 1000 parts, water 913, sugar 60, urea 6·5, salts, extractive matters, and uric acid 20·5. This patient made in volume about four times the healthy quantity of urine in twenty-four hours.

Urine in Dropsies.—In these diseases, particularly where associated

with disease of the kidneys, the urine is not increased in quantity; its specific gravity is very low, 1005 to 1015, and it contains but very little urea, but generally albumen, and sometimes caseüm. In these cases, the urea, which is deficient in the urine, is found in the serum of the blood and in the dropsical effusions. In some states of the system, which do not appear connected with any distinct disease, milk passes into the urine, in which as well the butter as the caseüm may be detected. Such cases have even been met with in males. In *jaundice* the colouring material of the bile passes abundantly into the urine, and may be detected by nitric acid. The natural elements of the urine are, however, not altered in quantity.

Blue and Black Urine.—The urine has been observed coloured deeply blue by a peculiar organic substance, which, however, has not been accurately examined. Braconnot found that it contained nitrogen, and was reddened by acids, and the colour restored by alkalies. But Sprangenberg found, in the case he observed, that acids dissolved the blue substance without changing its colour. Moncet observed in the urine of a child a black matter insoluble in water, but soluble in alkalies. Prout, who also observed this substance, termed it melanic acid.

In many states of the system, particularly in arthritic rheumatism, there is a great tendency to the formation of uric acid, and the urate of ammonia is deposited under the form of a crystalline precipitate when the urine cools. It is usually mixed with more or less of a yellowish-red body, which is not purpurate of ammonia (murexid), as Prout supposed, but a peculiar organic substance, soluble in alcohol, which deserves more minute examination. The deposition of this excess of matter in the joints and sheaths of the tendons, produces the *gouty concretions*, which consist, for the most part, of urate of soda.

In other conditions of the system, the formation of phosphatic salts predominates, and precipitates occur in the urine which are generally more crystalline and less highly coloured than those of uric acid or of urates. As these different conditions of the secreting organs require different modes of treatment, it is necessary to be able simply to distinguish between these two kinds of sediment. It is sufficient to remark, that the uric acid deposite is soluble in alkalies and insoluble in dilute acids, while the phosphatic sediments dissolve in dilute acids, but not in alkaline liquors, even though decomposed by them.

The uric acid and the inorganic salts of the urine are afterward deposited in the bladder, and form urinary calculi.

The *Uric Acid Calculus* is probably the most common. It is recognised by being decomposed by heat; being soluble in caustic alkalies, and precipitated by acids. When dissolved in nitric acid, evaporated and moistened with water of ammonia, it gives the rich purple colour of murexid.

The *Urate of Ammonia Calculus*, in addition to the characters of uric acid, gives off ammonia when dissolved in solutions of caustic potash.

The *Phosphate of Lime Calculus* fuses with difficulty, or not at all, before the blowpipe. It is dissolved by muriatic acid, and precipitated by caustic ammonia from this solution as a white powder not crystalline.

The *Ammoniaco-magnesian Phosphate Calculus* is generally crystalline in structure; before the blowpipe it gives off ammonia, and ulti-

mately melts, though with difficulty. It also gives off ammonia when boiled with caustic potash. It dissolves in dilute acids, and is precipitated as a crystalline powder on the addition of caustic ammonia.

The two latter calculi often form together, and produce the *Triple Phosphate*, or *Fusible Calculus.* This melts readily before the blowpipe, and if dissolved in a dilute acid, it gives with oxalic acid a precipitate of oxalate of lime, and then, with an alkali, a crystalline deposite of ammoniaco-magnesian phosphate.

All of these various deposites may occur in the bladder, either successively, and form the *Alternating Calculus,* or together, forming the *Mixed Calculus.* The recognition of these species will depend on the careful application of the methods by which each component may be known, as already described.

It is not very unfrequent to meet with calculi formed of materials which do not exist in healthy urine, but are produced by the decomposition of its natural constituents. Thus the *Mulberry Calculus,* so called from its usual external form, consists of oxalate of lime. When ignited it leaves caustic lime, which browns wet turmeric paper strongly, dissolves in muriatic acid, and is precipitated by adding oxalate of ammonia. Calculi have been found also, though rarely, consisting of carbonate of lime and of carbonate of magnesia.

The most remarkable calculi of this class, however, are those formed of the *Cystic Oxide* and *Xanthic Oxide,* substances of purely organic nature. The latter body is yellow, soluble in alkalies, and is precipitated by the addition of an acid. It dissolves in nitric and sulphuric acids, but not in muriatic or oxalic acids. Its formula is $N_4C_{10} . H_4O_4$. It contains, therefore, the same carbon, nitrogen, and hydrogen as uric acid, but less oxygen, whence the name *Uric Oxide* has been proposed for it. The *Cystic Oxide Calculus* consists of small yellow crystalline plates, which dissolve in alkalies, and crystallize out again on the addition of an acid, by an excess of which the cystic oxide is, however, redissolved. When heated strongly it is decomposed, evolving sulphurous acid and ammonia. It forms definite salts with the nitric and muriatic acids. Its formula is $N.C_6H_6 . O_4S_2$.

When blood is effused into the bladder, the fibrine is occasionally aggregated as a calculus, the recognition of which is very simple, from what has been said of the properties of fibrine (p. 663).

Those who would wish for more detailed information of the properties of calculi, and of the composition of the urine in health and disease, I would refer to the truly classical work of Doctor Prout on the Diseases of the Stomach and Urinary Organs.

SECTION V.

OF THE MILK, AND OTHER NATURAL AND MORBID PRODUCTS, NOT INCLUDED IN THE PRECEDING SECTIONS.

Some of the most remarkable constituents of milk have been already described, as lactic acid (p. 536), the sugar of milk (p. 535), the butter, fats (p. 589). It only remains to notice the general composition of milk, and the properties of the *Caseüm* or *curd.* It is well known that, by standing, milk abandons the greater part of its butter, which separates, with other substances, as *Cream.* Berzelius

found the cream from cows' milk to have specific gravity 1·0244, and to consist, in 100 parts, of 4·5 of butter, separated by agitation, 3·5 of caseüm, with some butter, separated by coagulation, and 92 of whey. The skimmed milk had a specific gravity of 1·0348, and contained in 100 parts:

Caseous matter with some butter	2·600	100·00.
Sugar of milk	3·500	
Alcoholic extract with lactic acid	0·600	
Chloride of potassium	0·170	
Alkaline phosphates	0·025	
Earthy phosphates and a trace of iron . .	0·230	
Water	92·875	

The following table presents the best results that have been as yet obtained on the average composition of the milk of different animals:

	Human.	Mares.	Asses.	Cows.	Sheep.	Dogs.
Specific gravity . .	1·0323	1·0395	1·0322	1·0320	1·0380	
Water	88·36	88·68	90·47	85·91	53·2	65·74
Extractive . .	1·24	. .	. .	. .	(Cream 11·5)	2·90
Caseïne	3·40	1·82	1·95	7·00	15·3	17·40
Butter	2·53	0·75	1·29	3·93	5·8	16·20
Sugar	4·25	8·75	6·29	2·87	4·2	
Ashes	0·22	. .	. .	0·29	. .	(Salts 1·50)

The butter of human milk is more solid than that of the cow, and appears to contain no butyrine.

The *Caseüm* or *Caseïne* is capable of existing in a soluble and an insoluble condition, like albumen. In milk it is principally dissolved, but a part insoluble, united with the butter, produces the emulsive appearance of the milk. On adding sulphuric acid to skimmed milk, the caseïne precipitates, combined with the acid, as a white coagulum, which, being washed with water so as to remove all adhering milk, and then digested with carbonate of barytes, the caseïne dissolves in the water, and may, by filtration, be freed from all traces of the butter, sulphuric acid, or barytes. The caseïne may also be precipitated by alcohol, and when the curd is digested with ether to remove all traces of butter, it may be looked upon as pure.

The solution of caseïne in water is thick, like mucilage; it smells as boiled milk, and dries down to an amber-coloured mass, which is again soluble in water. The solution is coagulated by all acids, even acetic acid, particularly when hot, and by alcohol. In relation to acids, caseïne is similar to albumen, except that to acetic acid; the constitution of its precipitates being precisely similar.

The coagulated condition of caseïne is not produced by boiling, but only by the digestive principle (rennet, pepsine), as already described (p. 679). When thus coagulated, caseïne is absolutely undistinguished from coagulated albumen in its properties. It contains a considerable quantity of bone-earth (phosphate of lime), amounting to five or six per cent., in intimate combination. Its organic element was found by Mulder to be proteine, of which ten atoms are combined with one of sulphur, the formula of caseïne being $C_{400}H_{310}.N_{50}O_{120}+S$. It contains no phosphorus, but to each atom so expressed, two atoms of bibasic phosphate of lime.

When coagulated caseïne containing water (cheese) is kept for

a long time, it undergoes a remarkable kind of decomposition, and a substance, crystallizable and soluble in water, is obtained, termed by Braconnot *Aposepedine.* By Mulder's experiments it appears, however, to be impure leucine (p. 667); and the *Caseous Oxide* and *Caseïc Acid* of Prout appear also to be the same bodies as have been already noticed as formed from the decomposition of the other proteïne substances.

By contact with caseïne, sugar of milk is rapidly converted into lactic acid, which precipitates the caseïne, without, however, really coagulating it; hence, on neutralizing the acid, the caseïne redissolves, and may react on a new quantity of sugar. In this manner Fremy has shown that the *Lactic Fermentation* may be carried on to an indefinite extent.

Constitution of Eggs.—The shell of hens' eggs consists of from 90 to 95 per cent. of carbonate of lime, one to five of phosphate of lime, and two to five of animal matter. Internally it is lined by a membrane analogous to epidermis. The white of egg is a concentrated solution of albumen, contained in the cells of a delicate membrane, in the centre of which the yolk is suspended. The nutritive material of the yolk consists of albumen and an oil; also a yellow colouring matter analogous to that of bile. The *Oil of Eggs* is obtained by expressing the egg boiled, and partly torrefied; it is reddish-yellow, thick, and solidified by cold; it soon becomes rancid; the solid portion of it appears to be cholesterine; the liquid contains phosphorus and nitrogen, and is not saponifiable. When the young animal is developed during incubation, the quantity of phosphoric acid in its bones is exactly represented by the quantity of phosphorus in the yolk and white; but as these bodies contain very little lime, that earth must be derived from the shell, which becomes thin and brittle as the animal advances in growth.

Liquor of the Amnios.—This fluid, in which the fœtus is immersed before birth, appears to be identical in constitution with the liquor effused from serous surfaces in dropsy (p. 671). The *Liquor of the Allantoïs* of the cow, which is really the urine of the fœtus, is of the same nature, but contains, in addition, a small quantity of allantoïn, the artificial formation of which is described p. 686.

Black Pigment of the Eye.—This substance is insoluble in water and alcohol. It is decomposed by strong acids and alkalies. Caustic potash dissolves it, forming a yellow liquor, from which acids throw down a clear brown powder. The action of nitric acid is nearly the same. The *Cuttle-fish Ink* has much analogy with the black matter of the eye, giving, when dried, a black powder, insoluble in water, alcohol, and ether, which dissolves in nitric acid and potash with a reddish-yellow colour, from which solution a yellowish powder falls when it is neutralized. The true nature of these black colouring matters, and their relation to the melanic acid of Prout, which sometimes appears in the urine, would deserve attentive study.

The Humours of the Eye consist of water, holding in solution albumen in small quantity, with the salts which usually accompany it. The crystalline lens consists of albumen, in a state of beautiful

and complex organization, amounting to about thirty-eight per cent. of the entire mass, which contains about sixty of water.

Cerumen. Wax of the Ear.—This substance contains an albuminous material insoluble in water, a solid and a liquid fat soluble in ether, and a deep yellow matter soluble in alcohol and insoluble in ether, to which its colour and very disgusting taste are due; another constituent, which appears to be peculiar to this secretion, is brown, insoluble in caustic potash; it most resembles horn in its properties, but is still quite distinct from that body.

Pus.—This remarkable morbid secretion has generally a specific gravity of 1·030. It consists of a clear liquor, in which float a great number of yellow globules, of various sizes, the largest of which are about twice the size of the globules of the blood. Pus loses by drying 86·1 of water in 100 parts, and hence contains 13·9 of solid material, from which alcohol takes 5·9 of fatty and extractive matters, and leaves 7·4 per cent. of a residue, which consists of coagulated albumen, the solid globules, and a substance peculiar to pus.

The globules of pus appear to consist of coagulated albumen. The serum contains two liquids, both coagulable by heat. One is albumen, the other *Pyin*, which is characterized by being coagulated both by heat, by acetic acid, and by a solution of alum. Güterbach, who has recently examined pus with great care, finds the only certain distinction between pus and mucus to be, that the pus globules sink always in water, while the mucus swims. If the suspected liquid be dried, the extraction of the fatty substance by ether should decide very positively.

Ambergris.—This substance, which is generally found floating on the seacoasts of tropical islands, is known to be an intestinal concretion of the spermaceti whale, analogous to the gallstones of cholesterine in other animals. Its principal ingredient is the *Ambreïne*, which is obtained by solution in boiling alcohol, whence it crystallizes, on cooling, in fine needles. It is white, tasteless, of a very agreeable odour; it is not saponifiable; its formula is $C_{33}H_{32}O$ By boiling with nitric acid it produces ambreïc acid, which crystallizes from its solution in alcohol in small colourless tables; it reddens litmus, but is scarcely soluble in water; it forms well-defined yellow salts with the alkalies; its formula appears to be $C_{20}H_{20}.N.O_{12}$.

SECTION VI.

OF THE PRESERVATION AND PUTREFACTION OF ANIMAL MATTERS.

From the greater complexity of composition of animal substances, their decomposition is more rapid, and its products more diverse, than in the case of organic bodies of vegetable origin; while the carbon, hydrogen, and oxygen give origin to the various kinds of ulmine and other substances of the same class, the nitrogen is generally evolved as ammonia, and the sulphur as sulphuretted hydrogen. It is the presence of these bodies that give to putrefying substances the disagreeable odour by which that process is distinguished from mere mouldering or rotting.

Even during life the constituent particles of the body are in a continual state of change, being absorbed and thrown out of the system, while others are assimilated in their place. Any part of our constituents, liquid or solid, which becomes unfitted for this vital function, is thereby killed, and must, if not got rid of, induce the death of the individual. Hence precisely the same means which give to animal substances the fixity of constitution which belongs to true chemical compounds, and thus preserve them from decomposition by the disturbing action of their own elements (as when we coagulate albumen by an acid, by corrosive sublimate, or by sulphate of copper), produce, if applied to the living body, the death of the part or of the whole being, by depriving the blood or the tissue of the mutability of constitution which is required for the functions of the animal frame.

It is thus that the generality of metallic poisons act in producing death. Being absorbed into the system, they unite with the albumen and fibrine of the blood, and, converting them into the insoluble compounds which we form in the laboratory, unfit them for the continual absorptive and secretive offices which, as organs, while they live they must fulfil. If the injury be local, and limited in extent, the part so coagulated may be thrown off, and after a certain time the functions return to their proper order. If the mass, or the importance of the affected parts be greater, the system cannot so get rid of the portions which have thus been removed from the agency of life to submit to merely chemical laws; on the contrary, the vital powers of the remaining portions of the animal are so much weakened in the effort that general death is caused.

For putrefaction it is thus necessary, 1st, that the force of vitality, which governs so completely the mere chemical tendencies of the elements of our tissues, be removed; 2d, that there shall not be present any powerful chemical reagent with which the organized material may enter into combination, and thus the divellant tendencies of the affinities of its elements be overcome; 3d, that water be present in order to give the necessary mobility; 4th, that oxygen be present, or at least some other gas, into the space occupied by which the gaseous products may be diffused; and, lastly, that the temperature shall be within moderate limits, putrefaction being impossible below 32° and above 182°.

The agency of the first of these preventive powers need not be farther noticed. The second is extensively employed in the preparation of bodies for anatomical purposes, by baths, or injections into the arteries, of solutions of corrosive sublimate, acetate of alumina, sulphate of iron, tannin, wood vinegar, and kreosote; this last body, however, does not appear to act by direct combinations, but by the complete (catalytic) coagulation it produces in all the tissues of the body that have proteïne for their base. The necessity for the presence of water is shown by the fact that, by drying the animal substances, they are completely preserved. It is thus that the bodies of those perishing in the Arabian deserts are recovered years subsequently, dried, but completely fresh. Alcohol and common salt act in preserving animal bodies by their affinity for water. If a piece of flesh be covered with salt, the water gradually passes from

the pores of the flesh, and, dissolving the salt, forms a brine, which does not wet the flesh (p. 540), but trickles off its surface; the water necessary for putrefaction is thus removed. The mode of strengthening alcohol in a bladder (p. 540) rests on the same principle. Fourth, by excluding oxygen, the putrefactive process is retarded, precisely as the fermentative action of the gluten in grape-juice (p. 538) cannot begin until a small quantity of oxygen be absorbed. It is thus that meat which is sealed up in close vessels, and then boiled for a moment, is preserved; the small quantity of oxygen of the air remaining then in the vessel is absorbed, and the product of that minute change being coagulated by the heat, it cannot proceed farther. A high temperature stops putrefaction by coagulating the azotized materials; a temperature below 32°, by freezing the water, acts as if the tissue had been dried; in both cases putrefaction is arrested.

During putrefaction, at a stage prior to any fetid gas being evolved, a peculiar organic substance is generated, possessed of intensely poisonous properties, and the blood of persons who have died from its effects is found to be quite disorganized and irritating when applied to wounds. The blood of over-driven cattle is found to produce effects similar to those of venomous reptiles, and the wounds received in dissection are sometimes followed by similar fatal consequences. The communication of disease in this way has recently been very ingeniously ascribed by Liebig to the general principle of the communication of decomposition by contact (p. 663). The small quantity of diseased organic matter originally introduced into the system by absorption, acts as a ferment, and reproduces itself in the mass of blood until this becomes unfitted for the performance of its functions, and the animal is killed; the active principle being thus copiously present, is exuded from the skin and lungs, and gives a contagious character to the disease, or it remains only in the blood, or is secreted in pustules, &c., constituting *infection,* by which the disease may be communicated to another person.

In the decomposition of vegetable matter in marshes, similar maleficent products may be evolved, and throwing the blood of the animal, by whom they are absorbed, into fermentative decomposition, produce the effects of *Malaria* and *Marsh Miasm.*

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